

ALMA MATER STUDIORUM · UNIVERSITÀ DI
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**Adiabatic and Local Approximations
for the Kohn-Sham Potential
in the Hubbard model**

Tesi di Laurea Magistrale

Relatore:
Chiar.mo Prof.
Fabio Ortolani

Presentata da:
Lorenzo Mancini

Correlatori:
Chiar.mo Prof. Cristian
Degli Esposti Boschi
Chiar.mo Prof. Rex
Godby

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Introduzione

Con l'avvento di tecnologie basate su dispositivi molecolari e la necessità di descrivere sistemi i componenti dei quali interagiscono con un ambiente time-dependent (TD), si è resa sempre più necessaria la determinazione di metodi *ab initio* che consentano di descrivere realisticamente sistemi elettronici correlati soggetti a campi esterni dipendenti dal tempo. La Density-functional theory [1, 2] si è dimostrata estremamente efficace nel descrivere le proprietà del ground-state di una grande varietà di sistemi differenti, basandosi spesso su approssimazioni locali quali la local-density approximation (LDA) [3]. Nella generalizzazione a sistemi tempo-dipendenti della teoria, la cosiddetta Time-Dependent Density Functional Theory (TDDFT) [4], la LDA è usata solitamente in approssimazione adiabatica e prende il nome di “adiabatic local-density approximation” (ALDA) [5].

Numerosi studi hanno dimostrato che approssimazioni di tipo ALDA sono in grado di descrivere correttamente solo un numero limitato di sistemi fisici tempo-dipendenti. Al contrario, risultano inefficaci in diverse situazioni [6, 7, 8, 9]. Dalle precedenti osservazioni, risulta evidente la necessità di approssimazioni più affidabili per il potenziale di scambio e correlazione in sistemi elettronici correlati tempo-dipendenti. In questo lavoro di tesi si è considerato il modello di Hubbard [10], nel quale l'interazione elettrone-elettrone presenta una forma semplice a corto raggio, con l'intento di ottenere risultati generalizzabili a sistemi elettronici correlati più realistici. In realtà, questo non è un compito facile. Infatti, un problema tutt'ora irrisolto della DFT è il diverso comportamento fra sistema continuo e reticolo. Questa

caratteristica, ad esempio, influenza negativamente l'applicabilità dei metodi DFT a sistemi come gli isolanti di Mott (dove la caratteristica di isolante è un effetto del reticolo e della densità opportunamente tarata) [11]. Questo modello può essere considerato in un certo qual modo il paradigma di un sistema elettronico fortemente correlato. Il suo principale vantaggio è che consente di trattare in modo piuttosto semplice sistemi correlati che non si prestano ad essere trattati altrettanto facilmente con le tipiche approssimazioni di fisica dello stato solido (come ad esempio la teoria dei liquidi di Fermi). Inoltre, la semplicità del modello rende possibile ottenere risultati affidabili per un numero discreto di elettroni interagenti ad un costo computazionale ragionevole [12].

In particolare, si è ottenuto l'esatto potenziale di Kohn-Sham tempo-dipendente V_{KS} per catene di Hubbard 1D, sottoposte a un campo esterno d.c. (direct current), utilizzando la densità elettronica e la densità di corrente ottenute dalla esatta evoluzione temporale del sistema a molti corpi. Si è quindi comparato l'esatto potenziale V_{xc} con due potenziali approssimati: un potenziale "adiabaticamente esatto" V_{xc}^{ad} ed un potenziale denominato "instantaneous ground state" V_{xc}^{igs} . Il primo dei due risulta dalla procedura usuale per ottenere potenziali approssimati adiabatici. Il secondo, che verrà trattato approfonditamente nel Capitolo 3, al contrario è una approssimazione meno comune, basata sul valore istantaneo del potenziale perturbante esterno. In questo lavoro di tesi si è analizzata l'efficacia di queste due approssimazioni. Inoltre, si sono considerate approssimazioni per il potenziale di scambio e correlazione V_{xc} e il suo gradiente basate sui valori locali di densità elettronica e densità di corrente. Dall'analisi di tali approssimazioni è stato possibile determinare che entrambe le suddette quantità fisiche sono lontane dal poter essere approssimate localmente. Infine, si sono studiati tramite la pair correlation function i rispettivi ruoli della correlazione del ground-state e di quella degli stati eccitati nel sistema dipendente dal tempo, relativamente a come queste sono legate ai potenziali.

Introduction

With the prospect of technologies based on molecular devices, and the necessity of being able to describe systems in which devices interact with a time-dependent (TD) environment, there is a need for *ab initio* methods to realistically describe correlated electronic systems subjected to TD external fields. Density-functional theory [1, 2] has proven to be an effective tool for describing ground-state properties of a great variety of different systems, often based on local approximations such as the local-density approximation (LDA) [3]. In the time-dependent generalization of DFT, TDDFT [4], the LDA is often used adiabatically (ALDA) [5].

Several studies have shown that the ALDA is able to describe properly only a limited range of time-dependent physical systems and that it frequently breaks down [6, 7, 8, 9]. There is a need for more reliable approximations for the exchange-correlation potential in time-dependent correlated electron systems. In this thesis work we consider the Hubbard model [10], in which the electron-electron interaction takes a simple short-range form, aiming to obtain insight which may be extended to more general correlated electron systems. Actually, this is not an easy task. In fact, there is a known issue related to the fact that DFT methods tend to behave quite differently when treating continuous or discrete systems. This feature, for example, affects negatively their performances when applied to systems such as Mott insulators (where the insulating characteristic is an effect of the lattice and of the properly tuned density) [11]. This model can be somehow considered as the paradigm of a strongly correlated electronic system. Its main advantage

is that it allows to treat in a quite simple way correlated systems, which cannot be easily handled with the approximations commonly used in solid state physics (e.g. the Fermi liquid theory). Moreover, the simplicity of the model means that reliable results may be obtained for substantial numbers of interacting electrons with reasonable computational effort [12].

In particular, we obtain the exact time-dependent Kohn-Sham potentials V_{KS} for 1D Hubbard chains, driven by a d.c. external field, using the time-dependent electron density and current density obtained from exact many-body time-evolution. The exact V_{xc} is then compared to two approximate potentials: the adiabatically-exact $V_{\text{xc}}^{\text{ad}}$ and the “instantaneous ground state” $V_{\text{xc}}^{\text{igs}}$. The former is obtained using the usual procedure for making adiabatic approximate potentials. The latter, which will be discussed in more detail in Chapter 3, is a less common approximation, based on the instantaneous value of the external perturbing potential. The effectiveness of these two approximations is analyzed. Moreover, approximations for the exchange-correlation potential V_{xc} and its gradient, based on the local density and on the local current density, are also considered and both physical quantities are observed to be far outside the reach of any possible local approximation. Finally, insight into the respective roles of ground-state and excited-state correlation in the time-dependent system, as reflected in the potentials, is provided by the pair correlation function.

Chapter 1

Density-functional Theory and Time-dependent Density-functional Theory

1.1 Density-functional theory (DFT)

1.1.1 General formulation

The original formulation of the density-functional theory (DFT) was proposed by Hohenberg and Khon (1964), and Khon and Sham (1965), as an approach to the ground state interacting fermions problem [1, 2], which consists in the solution of the static Schrödinger equation for a system of N interacting non-relativistic electrons,

$$\hat{H}\psi_j(\mathbf{x}_1, \dots, \mathbf{x}_N) = E_j\psi_j(\mathbf{x}_1, \dots, \mathbf{x}_N) \quad (1.1)$$

where ψ_j are the eigenfunctions of the Hamiltonian \hat{H} with corresponding energy eigenvalues E_j , and $\mathbf{x}_j = (\mathbf{r}_j, \sigma_j)$ is a shorthand notation for the space and spin coordinates of the j -th electron. Notice that equation (1.1) is the Schrödinger equation in the Born-Oppenheimer approximation. A more general formulation of the structure of matter would include along with the electronic degrees of freedom the nuclear ones.

The main idea of the theory, is that it is possible to define an auxiliary system (Kohn-Sham system) of the same number N of *non*-interacting electrons, moving in an effective potential $v_{\text{KS}}(\mathbf{r})$, which reproduce the *exact* ground-state electron density $n_0(\mathbf{x})$ of the real system of interacting electrons. If we consider a system of N particles in a state represented by the normalized wave function $|\psi\rangle$, the density of the system n_ψ is defined by the relation

$$n_\psi(\mathbf{x}) = \langle \psi | \sum_{i=1}^N \delta(\hat{\mathbf{q}}_i - \mathbf{x}) | \psi \rangle \quad (1.2)$$

$n_\psi(\mathbf{x})$ can therefore be viewed as the number of units of the system per unit volume: for any function $f(\mathbf{x})$,

$$\langle \psi | \sum_{i=1}^N f(\hat{\mathbf{q}}_i) | \psi \rangle = \int d\mathbf{x}^3 f(\mathbf{x}) n_\psi(\mathbf{x}) \quad (1.3)$$

Proof. We have

$$\begin{aligned} \langle \psi | \sum_{i=1}^N f(\hat{\mathbf{q}}_i) | \psi \rangle &= \int d\mathbf{x}^3 f(\mathbf{x}) \langle \psi | \sum_{i=1}^N \delta(\hat{\mathbf{q}}_i - \mathbf{x}) | \psi \rangle \\ &= \int d\mathbf{x}^3 f(\mathbf{x}) n_\psi(\mathbf{x}) \end{aligned} \quad (1.4)$$

Further, n_ψ satisfies the normalization condition

$$\int d\mathbf{x}^3 n_\psi(\mathbf{x}) = N \quad (1.5)$$

Proof. The equality follows from the definition, using $f(\mathbf{x}) = 1$

For a system of N interacting electrons described by the total Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} + \hat{W}, \quad (1.6)$$

where \hat{T} is the kinetic-energy operator

$$\hat{T} = - \sum_{j=1}^N \frac{\nabla_j^2}{2}, \quad (1.7)$$

\hat{V} is the potential operator

$$\hat{V} = \sum_{j=1}^N v(\mathbf{r}_j), \quad (1.8)$$

and \hat{W} is the operator for the electron-electron interaction

$$\hat{W} = \frac{1}{2} \sum_{\substack{j,k \\ j \neq k}}^N w(|\mathbf{r}_j - \mathbf{r}_k|), \quad (1.9)$$

the electron density, or the number of electrons per unit volume, can be written as

$$n(\mathbf{r}, t) = N \int |\psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N, t)|^2 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N, \quad (1.10)$$

Proof. This follows from the fact that the probability of finding electron one in \mathbf{r} :

$$|\psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N, t)|^2 \quad (1.11)$$

equals the probability of finding any of the other electrons $(\mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)$ in the same coordinate. So, it is sufficient to multiply this probability for the number of electrons N .

Hohenberg and Khon showed how the knowledge of the ground-state charge density n_0 , along with the number of particles (which is just the integral of the density), allows to determine essentially all the properties of the system and, in particular, the ground-state energy E_0 of the system. The great advantage of the density-functional approach is that, using only the information of n , it does not require the computation of the full wave-function ψ (which contains vastly more information than the one needed) in order to obtain all the properties of interest. Before proceeding in the analysis of the theory, let us review the variational principle, which will be fundamental for proving the Hohenberg-Khon theorem:

Let us consider the wave-function ψ and the Hamiltonian \hat{H} :

1. *$\langle \psi | \hat{H} | \psi \rangle$ is a minimum when $|\psi\rangle = |\psi_0\rangle$, where $|\psi_0\rangle$ is the exact ground-state function.*
2. *if $|\psi\rangle = |\psi_0\rangle + |\alpha\rangle$, then the difference between the expectation value of \hat{H} and the ground-state energy E_0 satisfies*

$$\langle \psi | \hat{H} | \psi \rangle - E_0 \propto |\alpha|^2 \quad (1.12)$$

3. *if $|\psi\rangle = |\psi_n\rangle$, where $|\psi_n\rangle$ is the n -th excited state of \hat{H} ; then the expectation value $\langle \psi | \hat{H} | \psi \rangle$ is stationary with respect to variations in ψ*

Proof. Considering the completeness property, let us write the general wave-function ψ as a linear combination of exact eigenfunctions of \hat{H} (which are the elements of a basis set for the Hilbert space of infinite dimensions),

$$|\psi\rangle = \sum_{i=0}^{\infty} c_i |\phi_i\rangle. \quad (1.13)$$

Using equation (1.13) in the expectation value we obtain:

$$\langle \psi | \hat{H} | \psi \rangle = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} c_i^* c_j \langle \phi_i | \hat{H} | \phi_j \rangle = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} c_i^* c_j E_i \delta_{ij} \quad (1.14)$$

$$= \sum_{i=0}^{\infty} |c_i|^2 E_i \quad (1.15)$$

$$= \sum_{i=0}^{\infty} |c_i|^2 (E_i - E_0) + E_0 \sum_{i=0}^{\infty} |c_i|^2 \geq E_0, \quad (1.16)$$

where in the third passage we summed and subtracted $E_0 \sum_{i=0}^{\infty} |c_i|^2 = E_0$. The last relation follows simply from the normalization condition $\sum_{i=0}^{\infty} |c_i|^2 = 1$. Easily we see that, if $|\psi\rangle = |\psi_0\rangle$, in eq. (1.16) the equality holds, and the first part of the principle is proved. Also the second point follows automatically from (1.16) (2-nd order error in $\psi(c_1, c_2, \dots)$).

The core of density-functional theory is the Hohenberg-Khon theorem. We consider here the original version of the theorem, which assumes that the ground state of the system is not degenerate:

In a finite system of N interacting electrons with a given particle-particle interaction there exist a one-to-one correspondence between the external potential $v(\mathbf{r})$ and the ground-state density $n_0(\mathbf{r})$. In other words, the external potential is, up to an arbitrary additive constant, a unique functional of the ground-state density, $v[n_0](\mathbf{r})$.

Proof. The proof proceeds in two steps via *reductio ad absurdum*. In the first step, we note that two different potentials (the potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$ are considered different if they are not related by a constant shift $v'(\mathbf{r}) \neq v(\mathbf{r}) + c$) cannot produce the same ground-state function or, in other words, ψ_0 and ψ'_0 must differ for more than a phase factor. In fact, if we assume that ψ_0 and ψ'_0 are the same, subtracting the Schrödinger equations, one obtains

$\hat{V} - \hat{V}' = E_0 - E'_0$, in contradiction with the requirement that $v'(\mathbf{r}) \neq v(\mathbf{r}) + c$. The relationship between potentials and wave-function is therefore unique ¹. In the second part of the proof, we show that two different ground-state wave-function produce different ground-state densities. The proof follows directly from the variation principle: let us consider the ground-state energy associated with $v'(\mathbf{r})$,

$$E'_0 = \langle \psi'_0 | \hat{H}' | \psi'_0 \rangle, \quad (1.17)$$

and the fact that ψ_0 is different from ψ'_0 . If we assume that both ψ_0 is different from ψ'_0 produce the same density, we have

$$E'_0 < \langle \psi_0 | \hat{H}' | \psi_0 \rangle = \langle \psi_0 | \hat{H} + \hat{V}' - \hat{V} | \psi_0 \rangle \quad (1.18)$$

$$= E_0 + \int d^3r [v(\mathbf{r}) - v'(\mathbf{r})] n_0(\mathbf{r}). \quad (1.19)$$

Note that we can write an analogue expression simply interchanging primed and unprimed quantities,

$$E_0 < \langle \psi'_0 | \hat{H} | \psi'_0 \rangle = \langle \psi'_0 | \hat{H} + \hat{V}' - \hat{V} | \psi'_0 \rangle \quad (1.20)$$

$$= E'_0 + \int d^3r [v'(\mathbf{r}) - v(\mathbf{r})] n_0(\mathbf{r}). \quad (1.21)$$

Next, summing equations (1.18) and (1.20), we obtain

$$E_0 + E'_0 < E_0 + E'_0, \quad (1.22)$$

which is obviously contradictory.

The Hohenberg-Kohn theorem does not only establish a one-to-one correspondence between external potentials and ground-state densities, it also contains two important corollaries related to the total energy functional

$$E_{v_0}[n] = \langle \psi | \hat{T} + \hat{V}_0 + \hat{W} | \psi \rangle. \quad (1.23)$$

¹Actually, a unique relationship is no longer guaranteed if generalization of DFT, as for example spin-DFT and current-DFT, are considered. However this does not affect the results of theorem because the second step of the proof still goes through.

These can be shown restating the theorem in this way:

In a finite system of N interacting electrons subjected to an external potential $v_0(\mathbf{r})$. There exist an universal functional of the charge density $F[n]$, such that the functional

$$E[n] \equiv F[n] + \int n(\mathbf{r})v_0(\mathbf{r})d\mathbf{r}^3 \quad (1.24)$$

is minimized for $n = n_0$ and $E[n_0] = E_0$

Proof. For proving the theorem we start defining the operator

$$\hat{F} = - \sum_{i=1}^N \frac{\nabla_i^2}{2} + \sum_{\langle i,j \rangle} u(|\mathbf{r}_i - \mathbf{r}_j|), \quad (1.25)$$

where the sum in the second term is between pairs of the i -th and j -th electrons, with $i \neq j$. Note that the operator \hat{F} satisfies the equation

$$\hat{H} = \hat{F} + \sum_{i=1}^N v_0(\mathbf{r}_i). \quad (1.26)$$

Next we define the functional

$$F[n] = \min_{\psi \rightarrow n(\mathbf{r})} \langle \psi | \hat{F} | \psi \rangle, \quad (1.27)$$

where the functional minimum is searched between all the N -electrons wave-functions ψ which yields the density $n(\mathbf{r})$. We can write the functional $E[n]$ as

$$E[n] \equiv F[n] + \int n(\mathbf{r})v_0(\mathbf{r})d\mathbf{r}^3 \quad (1.28)$$

$$= F[n] + \langle \psi | \sum_{i=1}^N v_0(\mathbf{r}_i) | \psi \rangle. \quad (1.29)$$

For each density n , let ψ_n be the wave-function that minimizes $F[n]$. Then

$$E[n] = \langle \psi_n | \hat{F} | \psi_n \rangle + \langle \psi_n | \sum_{i=1}^N v_0(\mathbf{r}_i) | \psi_n \rangle = \langle \psi_n | \hat{H} | \psi_n \rangle. \quad (1.30)$$

Let ψ_0 be the actual ground-state wave-function of this system, with density n_0 . Then, from the variational principle follows that

$$\langle \psi_n | \hat{H} | \psi_n \rangle \geq E_0 \quad (1.31)$$

for any function n , but also

$$\langle \psi_{n_0} | \hat{F} | \psi_{n_0} \rangle \leq \langle \psi_0 | \hat{F} | \psi_0 \rangle, \quad (1.32)$$

which yields

$$\langle \psi_{n_0} | \hat{H} | \psi_{n_0} \rangle \leq \langle \psi_0 | \hat{H} | \psi_0 \rangle = E_0. \quad (1.33)$$

Thus, $E[n_0] = E_0$ and $E[n] \geq E_0$ for any n .

This variational property of $E[n]$ allows to compute the ground-state density n_0 of an interacting N -electron system using the Euler equation

$$\frac{\delta}{\delta n(\mathbf{r})} \left[E[n] - \mu \int d^3r' n(\mathbf{r}') \right] = 0, \quad (1.34)$$

where μ is a Lagrange multiplier that ensure the correct total number of electrons. Equation (1.34) can then be written in term of the functional $F[n]$,

$$\frac{\delta F[n]}{\delta n(\mathbf{r})} + v_0 = \mu. \quad (1.35)$$

In the original formulation of density-functional theory by Hohenberg and Kohn, $E[n]$ is defined only for those densities $n(\mathbf{r})$ that are actual ground-state densities belonging to some external potential. These functions $n(\mathbf{r})$ are called *v-representable*. The v-representability is a formal issue still not completely resolved. To some extent, most of the difficulties related to the domain of the functional $E[n]$ have been overcome with the formalism showed in the latter formulation of the Hohenberg-Kohn theorem, which consist in the definition of the universal functional

$$F[n] = \min_{\psi \rightarrow n} \langle \psi | \hat{T} + \hat{W} | \psi \rangle. \quad (1.36)$$

This is commonly referred to as the *constrained search* formalism [13]. Its main advantage is that it provides an operational definition of the universal functional $F[n]$ in the form of a constructive procedure. even if this procedure plays an important formal role in DFT, it is not really practical. In fact computing $F[n]$ (which involves a search over an infinite value of wave-function) is essentially always more costly than solving the Schrödinger equation for N electrons.

For making DFT practical, is necessary to consider the formulation proposed by Kohn and Sham, which consist in the redefinition of the functional $E[n]$:

$$E[n] = T_S[n] + \int n(\mathbf{r})v_{\text{eff}}(\mathbf{r})d\mathbf{r}^3 \quad (1.37)$$

where $T_S[n]$ is the kinetic energy of the non-interacting electrons and

$$v_{\text{eff}} = v(\mathbf{r}) + \int n(\mathbf{r}')u(|\mathbf{r} - \mathbf{r}'|)d\mathbf{r}'^3 + \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (1.38)$$

Proof. Eq. (1.37) is obtained considering the expression for $E[n]$,

$$\begin{aligned} E[n] = & T_S[n] + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' n(\mathbf{r})n(\mathbf{r}')u(|\mathbf{r} - \mathbf{r}'|) \\ & + E_{xc}[n] + \int d^3\mathbf{r}n(\mathbf{r})v(\mathbf{r}), \end{aligned} \quad (1.39)$$

where the functional $F[n]$ has been divided into three separate terms: the kinetic energy of a non interacting N -electron system $T_S[n]$, an Hartree-like term which takes into account the electrostatic potential energy of n , and the exchange-correlation energy $E_{xc}[n]$. Eq. (1.38) follows directly from

$$\int d^3\mathbf{r}n(\mathbf{r})\frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} = E_{xc}[n]. \quad (1.40)$$

From equations (1.37) and (1.38) it is easy to see that the system can be treated as if it consists of N non interacting electrons moving in the effective potential v_{eff} . Thus, it is sufficient to solve N one particle Schrödinger equations for a system of non-interacting electrons subjected to the effective potential

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i + v_{\text{eff}}\psi_i = \varepsilon_i\psi_i. \quad (1.41)$$

From here the electron density is simply obtained:

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi(\mathbf{r})|^2. \quad (1.42)$$

Note that the set of equation (1.41) has to be solved self-consistently (similarly as in the Hartree-Fock approach to the many particle problem), due to the dependence of the effective potential in the Schrödinger equations on the electron density. The effective potential, which has been shown to be the sum of three contribution, is commonly referred to as the Kohn-Sham potential

$$v_{\text{KS}} \equiv v_{\text{eff}} = v_{\text{ext}} + v_{\text{Hartree}} + v_{\text{xc}} \quad (1.43)$$

where the Hartree potential is the functional derivative of the interaction energy, while the exchange-correlation potential is given by the functional derivative of the exchange-correlation energy:

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})} \quad (1.44)$$

and E_{xc} is itself a functional of the electron density $n(\mathbf{r})$.

This then closes the relationship between the KS system and the original physical problem. Once $E_{\text{xc}}[n]$ is known, $v_{\text{xc}}(\mathbf{r})$ is determined by differentiation. The KS equations can be solved self-consistently and the total energy found from the total energy functional. There is yet still one issue to be considered: density-functional theory as it has been stated here is in principle exact. Unfortunately however, neither $E_{\text{xc}}[n]$ nor $v_{\text{xc}}[n]$ are actually known and both need to be approximated. We will show in the next section that it is possible to consider several different types of approximations of varying accuracy and computational cost.

1.1.2 Approximate functionals

In any ground-state DFT calculation, an approximate model for the functional $E_{xc}[n]$ has to be devised. There exist a hierarchy of these approximated functionals. Actually, it is still not known a functional which is better than the others for any case, but it is necessary to work them out depending on the system under study. KS functionals can be divided into three types. The simplest of these is the local density approximation (LDA) [3], where the exchange-correlation energy at a point (\mathbf{r}') is calculated as if it were a uniform electron gas

$$E_{xc}[n] \simeq \int \varepsilon_{xc}(n(\mathbf{r}))n(\mathbf{r})d^3\mathbf{r} \quad (1.45)$$

where ε_{xc} is the exchange-correlation energy per electron in a homogeneous electron gas. In general, LDA works remarkably well, given the vast difference between homogeneous electron gases and atoms or molecules, for the determination of ground state energies for a wide range of systems; even if total energies are generally underestimated. The logical improvement of LDA is the generalized gradient approximation (GGA), in which information about how rapidly the density is changing is included via its gradient

$$E_{xc}[n] \simeq \int \varepsilon_{xc}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla \nabla n(\mathbf{r}) \dots)n(\mathbf{r})d^3\mathbf{r}, \quad (1.46)$$

ε_{xc} being some phenomenological energy function. The simplest of these, originally proposed by Kohn and Sham in 1965 [2], is the gradient expansion approximation (GEA), which is found by examining the slowly varying limit of the electron gas. However, GEA usually fails to improve the accuracy of LDA. Later, more accurate GGA's, which reduces to LDA for the uniform electron gas and that satisfies more exact conditions, were constructed. Finally, the last type of approximation are Hybrid functionals which consider within a GGA scheme a fraction of the exact exchange (e.g. considering experimentally fitted parameters).

1.2 Time-dependent density-functional theory (TDDFT)

Density-functional theory has proved to be an efficient method for treating stationary systems in a wide range of many-body problems. The necessity of having a good tool also for time dependent problems treated in terms of density functionals, has lead to a generalization of the theory to the time-dependent case and so, to the formulation of time-dependent density-functional theory (TDDFT). In order to define such theory, it is necessary to find a theorem, comparable to the Hohenberg and Kohn one [1], that can be demonstrated for arbitrary TD systems. This result was achieved by E. Runge and E. K. U. Gross, whom proved the homonymous theorem [4] that we state here:

Consider N non-relativistic electrons, mutually interacting via the Coulomb repulsion, in a time-dependent external potential. Densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$ evolving from the same initial state $\psi(t = 0)$ under the influence of two external potentials $v_{\text{ext}}(\mathbf{r}, t)$ and $v'_{\text{ext}}(\mathbf{r}, t)$ (both Taylor expandable about the initial time 0) are always different provided that the potentials differ by more than a purely time-dependent (r -independent) function:

$$\Delta v_{\text{ext}}(\mathbf{r}, t) \neq c(t), \quad (1.47)$$

where

$$\Delta v_{\text{ext}}(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) - v'_{\text{ext}}(\mathbf{r}, t). \quad (1.48)$$

Thus there is a one-to-one mapping between densities and potentials, and the time-dependent potential is a functional of the time-dependent density (and the initial state).

Proof. Let $v_{\text{ext}}(\mathbf{r}, t)$ and $v'_{\text{ext}}(\mathbf{r}, t)$ two potentials which satisfies the condition (1.47). This does of course not exclude that the potentials are identical at

$t = t_0$. However, since the potentials can be expanded into a Taylor series around t_0 , there must exist some minimal nonnegative integer k such that

$$\frac{\partial^k}{\partial t^k}(v_{\text{ext}}(\mathbf{r}, t) - v'_{\text{ext}}(\mathbf{r}, t)) \neq \text{const.} \quad (1.49)$$

For proving the theorem, one has to show that the two densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$ corresponding to $v_{\text{ext}}(\mathbf{r}, t)$ and $v'_{\text{ext}}(\mathbf{r}, t)$ are different if (1.49) holds for some $k \geq 0$. Firstly, we show that the corresponding current densities differ. In order to do this, we consider the current density $J(\mathbf{r}, t)$ given by

$$J(\mathbf{r}, t) = \langle \psi(t) | \hat{J}(\mathbf{r}, t) | \psi(t) \rangle \quad (1.50)$$

where

$$\hat{J}(\mathbf{r}, t) = \frac{1}{2i} \sum_{j=1}^N (\nabla_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \nabla_j) \quad (1.51)$$

is the current density operator. The equation of motion for the difference of the two current densities gives:

$$\left. \frac{\partial \Delta J(\mathbf{r}, t)}{\partial t} \right|_{t=0} = -n_0(\mathbf{r}) \nabla \Delta v_{\text{ext}}(\mathbf{r}, 0) \quad (1.52)$$

If the potentials differ at $t = t_0$ (i.e., if (1.49) holds for $k = 0$) then the right-hand side of this equation will be different from zero and thus $J(\mathbf{r}, t)$ and $J'(\mathbf{r}, t)$ will become different infinitesimally later than t_0 . This is true even if the minimum integer k for which (1.49) holds is greater than zero. In general, If the Taylor-expansion about t_0 of the difference of the two potentials is not spatially uniform for some order, then the Taylor-expansion of the current density difference will be non-zero at a finite order. This establishes that the external potential is a functional of the current density, $v_{\text{ext}}[J, \psi_0](\mathbf{r}, t)$. Next one has to show that the potential is a functional of density and of the initial wave-function, $v_{\text{ext}}[n, \psi_0](\mathbf{r}, t)$. We shall achieve this considering continuity:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot J(\mathbf{r}, t) \quad (1.53)$$

which leads to

$$\left. \frac{\partial^2 n(\mathbf{r}, t)}{\partial t^2} \right|_{t=0} = \nabla \cdot (n(\mathbf{r}, 0) \nabla \Delta v_{\text{ext}}(\mathbf{r}, 0)). \quad (1.54)$$

The functional dependence on n is showed imposing some boundary conditions: it has been shown that

$$\int d^3\mathbf{r} \Delta v_{\text{ext}}(\mathbf{r}, 0) \nabla \cdot (n_0(\mathbf{r}) \nabla \Delta v_{\text{ext}}(\mathbf{r}, 0)) = \int d^3\mathbf{r} [\nabla \cdot (\Delta v_{\text{ext}}(\mathbf{r}, 0) n_0(\mathbf{r}) \nabla \Delta v_{\text{ext}}(\mathbf{r}, 0)) - n_0 |\nabla \Delta v_{\text{ext}}(\mathbf{r}, 0)|^2]. \quad (1.55)$$

Note that the first term on the right vanishes for physically realistic potentials (due to the Green's theorem), while the second term is negative, so if $v_{\text{ext}}(\mathbf{r}, 0)$ is non-uniform, the integral must be finite, causing the densities to differ in 2nd order in t . This argument applies to each order and the densities $n(\mathbf{r}, t)$ and $n'(\mathbf{r}, t)$ are going to become different infinitesimally later than t . This proves $v_{\text{ext}}(\mathbf{r}, t) = v_{\text{ext}}[n, \psi_0](\mathbf{r}, t)$

It has been shown [14] that if the initial state is chosen to be a non-degenerate ground-state, the potential $v_{\text{ext}}(\mathbf{r}, t)$ is a functional of the density $n(\mathbf{r}, t)$ alone, due to the Hohenberg-Kohn theorem [1]. Thus, we can simply write $v_{\text{ext}}[n](\mathbf{r}, t)$.

The Runge-Gross theorem allows to write the time-dependent Kohn-Sham equations

$$i \frac{\partial \psi_j(\mathbf{r}, t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\right) \psi_j(\mathbf{r}, t) + v_{\text{KS}}(\mathbf{r}, t) \psi_j(\mathbf{r}, t), \quad (1.56)$$

whose potential is uniquely chosen for reproducing the exact (of the interacting system) electron densities:

$$n(\mathbf{r}, t) = \sum_{j=1}^N |\psi_j(\mathbf{r}, t)|^2 \quad (1.57)$$

The expression of the KS potential seen for ground-state density-functional theory(1.43) still holds. But, in this case, it is necessary to consider memory effects. In fact, in this case the exact exchange-correlation potential $v_{\text{xc}}(\mathbf{r}, t)$, which is defined by equation(1.43), is known to be a functional of the electron

density $n(\mathbf{r}, t)$ at all points and at all non-future times $v_{xc}(\mathbf{r}, t)[n]$ (in general $v_{xc}(\mathbf{r}, t)$ would not only be a functional of the density, but also of the initial state wave-functions of the interacting system and of the non-interacting one. However, if both initial states are chosen to be non-degenerate ground-states, respectively of the interacting and non-interacting system, the exchange-correlation potential becomes a simple functional of the density alone.)

As for in ground-state density functional theory, time-dependent density-functional theory is in principle exact, but the functional $v_{xc}[n]$ is not known and need to be approximated. Fortunately, there exist a natural way for obtaining approximate functionals from the ones for the time-independent case. In fact, any ground-state approximation (LDA, GGA, hybrid) automatically provides an adiabatic approximation for use in TDDFT. We will treat these approximate functionals in more detail in Chapter 3.

Chapter 2

Hubbard model

2.1 Hubbard model Hamiltonian and properties

The Hubbard model was proposed by J. Hubbard in 1963, with the initial aim of understanding the behaviour of those transition metal monoxides which had been predicted to be metals using the usual methods, but that experimentally showed an anti-ferromagnetic insulating behaviour. The characteristic that allowed the Hubbard model to be more suitable for treating such systems was essentially the more careful treatment of strong interactions. Even if the model proposed by Hubbard is an highly oversimplified one, it allows to yield both band-like and localized behaviour of the electrons in a lattice in suitable limits. The first assumption made by the Hubbard model is that for each ion of the lattice is considered only a single localized orbital level and all the other bound and continuum electron levels are neglected. With this simplification the state of the model is simply given: for each ion is sufficient to consider the four possible electron configurations consistent with the Pauli exclusion principle (empty level, one electron with either spin up or down, two electrons with opposite spin). The second assumption made by Hubbard in his model is related to the interaction between electrons: electrons which have the possibility to move around in

the lattice would obviously experiment a screened Coulomb interaction due to other electrons. For simplicity, in the Hubbard model is considered only the Coulomb repulsive interaction which occurs between electrons occupying the same site. So, the interaction between electrons on different sites is neglected. With these assumptions the Hamiltonian of the model contains a set of terms diagonal in the considered states, consisting in a positive energy U times the number of doubly occupied ionic levels plus an energy ε times the number of electrons, and an off-diagonal set of terms which have matrix elements different from zero only for those couples of states that represent the movement of one electron from one site to an adjacent one, without changes for what concern the spin state. The energy scale that govern this hopping process is defined t and is determined by the overlapping of the different wave functions. Considering the exponential decay of the electronic wave-functions, allowing the hopping only between adjacent sites is a reasonable approximation. Actually, nothing prevents us from including the effect of Coulomb interaction between particles on different sites. In this case the model system is often referred to as *extended Hubbard model*.

In a second quantization point of view, the Hubbard Hamiltonian can be formalized in the following expression:

$$\hat{H} = \varepsilon \sum_{R,\sigma} \hat{n}_{R,\sigma} + U \sum_R \hat{n}_{R\uparrow} \hat{n}_{R\downarrow} - t \sum_{\langle RR' \rangle \sigma} \hat{\Psi}_{R\sigma}^\dagger \hat{\Psi}_{R'\sigma} + \sum_{R\sigma} V_R^{\text{ext}}(\tau) \hat{n}_{R\sigma}. \quad (2.1)$$

In Eq. (2.1), $\hat{\Psi}_{R\sigma}^\dagger$ and $\hat{\Psi}_{R'\sigma}$ are respectively the creation and annihilation operators for one electron which position and spin state are indexed by R and σ , and $\hat{n}_{R\sigma} = \hat{\Psi}_{R\sigma}^\dagger \hat{\Psi}_{R\sigma}$ is the corresponding number operator. $\langle RR' \rangle$ denotes nearest-neighbour sites (we are not considering the extended Hubbard model), $\sigma = +1, -1$ and $V_R^{\text{ext}}(\tau)$ is a general time-dependent potential. Even with these simplifications, the model can be too difficult for exact analysis for a large number of sites. However, it can be really useful for obtaining information about particular systems, as we will see in the next paragraphs.

The original model proposed for fermions (electrons) has strong similarities with the so-called *tight binding approximation* from solid state physics

(if we remove the term in U in (2.1), we obtain the simpler tight binding Hamiltonian from regular band theory). The main feature of the latter approximation is to consider, within a mean-field approximation, the possibility of hopping between atoms for the electrons, which are viewed as occupying the standard orbitals of their constituent atoms. While the hopping process is described mathematically has a “hopping integral” between neighbour atoms (causing the formation of electronic bands in crystalline materials, due to overlapping between atomic orbitals), the Coulomb interactions between electrons is not considered explicitly; but the effect of these interactions is approximated considering an average potential due to the nuclei and other electrons, acting on non-interacting electrons. On the contrary, the Hubbard model includes explicitly the so-called “on-site repulsion”, due to the Coulomb interaction between two electrons on the same orbital. Now, this allows to study the competition between the two different energy scales t , which is a function of the distance and angles between neighbouring atoms, and U , which is no longer hidden in the average potential. The ratio U/t is at the base of the usefulness of the model for explaining transitions phenomena, as the transitions from metal to insulator in transition metal oxides (*Mott insulators*) due to heating, or the transition from conductor to insulator in systems where the increase of the atomic number causes an increase of the lattice parameter, changing the former ratio.

The behaviour of Hubbard systems is strongly dependent on the “filling” of the system itself. We define a system to be in the *half filling configuration* when the number of electrons equals the number of sites. For $U \ll t$, when there is less than half filling, the system will avoid configurations with doubly occupied sites (each doubly occupied site costs an additional energy U). Similarly, when there is more than half filling the system avoids empty sites (an empty site implies one more doubly occupied site). In the limit of large U the half filling case is special: there is one electron located at each site and interactions between different sites take place through virtual double occupation. in this case the system acts like an insulator.

In one-dimensional half-filled chains the ground state is insulating for all values of $U > 0$. The case of one dimension is also the only one for which there is an exact solution of the Hubbard Hamiltonian. It was solved exactly by Lieb and Wu [15] and, for half filling, the following analytic form for the ground-state energy per electron E_0/N , in the limiting case of $N \rightarrow \infty$, was derived:

$$\lim_{N \rightarrow \infty} \frac{E_0}{N} = -4|t| \int_0^\infty \frac{dx J_0(x) J_1(x)}{x [1 + \exp(xU/|t|)]}, \quad (2.2)$$

where $J_i(x)$ are Bessel functions. Moreover, considering the solution of the Hubbard model obtained using the *Bethe ansatz technique* [16], it is possible to derive the explicit form of the ground-state wave-function $\psi(x_1, \dots, x_N)$, where indexes $1, \dots, M$ are for the coordinates of spin-up electrons and $M + 1, \dots, N$ are those of the spin-down electrons. In the limit $U \rightarrow \infty$, the wave-function factorizes into

$$\psi(x_1, \dots, x_N) = \det |e^{ik_j x_j}| \phi(y_1, \dots, y_M). \quad (2.3)$$

Here, the first part is a Slater determinant of non-interacting fermions describing the charge degree of freedom. The second part $\phi(y_1, \dots, y_M)$ is the exact solution of a 1D Heisenberg spin chain and (y_1, \dots, y_M) are pseudo-coordinates of the spin-down electrons. The factorization of (2.3) in one part involving charge degrees of freedom and another one involving only spin degrees of freedom is one of the most characteristic aspects of the Hubbard model. The same separation appears also in the excitations and has been shown to be a general feature of strongly correlated electronic systems.

Recently, the Hubbard model, or more precisely the *Bose-Hubbard model* [17] (which is closely related to the Hubbard model, but it allows to describe interacting bosons on a lattice instead of fermions), has proven to be an important tool for describing ultracold atoms in optical lattices. these systems in their turn are known to be a versatile tool for applications like quantum information processing and quantum simulation. In these applications, is fundamental the ability to control interatomic interactions and this control is achieved through *Feshbach resonances* [18]. A significant feature of these

system is the possibility of fixing a negative effective value of the interaction U , in contrast with solid state bulk systems, in which the interaction value is necessarily determined by the ordinary repulsive Coulomb interaction.

2.2 (TD)DFT applications to the Hubbard model

We have seen in the previous paragraph that the Hubbard model shows some typical features of strongly correlated systems. The strong correlation of the model can easily be proved in one-dimensional Hubbard chains showing that they do not represent Fermi liquids (see Chapter 3). This statement can be proved studying the momentum distribution function $n(p)$. It is possible to show that it does not have a discontinuity at p_F , but rather a singularity [19]. This implies that the system does not have a Fermi surface in the usual sense. Actually, the behaviour of $n(p)$ corresponds to that found for other solvable model Hamiltonians for one-dimensional electronic systems and the system is usually referred to as a *Tomonaga-Luttinger liquid* [20]. The latter is the paradigm for 1D systems, which takes the place of the ordinary Fermi liquid commonly used for 3D systems.

The way in which the Hubbard model treats correlations is one of its most appealing features in order to study DFT and TDDFT functionals. In fact, the Hubbard model is the simplest model of a strongly correlated system. The possibility of working in a discrete system instead of a continuous one, and of considering the interaction only between electrons on the same orbital, can dramatically simplify the task of understanding the way in which DFT and TDDFT functional depends on electron correlation (aside from allowing to reduce greatly the computational burden with respect to a more realistic system with the same number of atoms). Hubbard systems have been considered by Verdozzi [12] for providing a characterization of TDDFT for strongly correlated systems.

Chapter 3

Adiabatic theorem

3.1 Original formulation and proof of the adiabatic theorem

In studying many-body time-dependent systems, one is obviously interested in knowing the way in which the wave-function that describes the state of the system changes during the time evolution, when the particles are subjected to a varying external potential. In chapter 5 we will treat more exhaustively the time dependence of wave-functions. For now, we will content ourselves with looking at two limiting cases: in general, the time evolution depends critically on the time T during which the modification of the Hamiltonian takes place. The first case of interest is when T is very small, thus the Hamiltonian is subjected to a sudden change. The second one, is when T is very large, and the Hamiltonian is subjected to a so-called *adiabatic change*. We suppose the Hamiltonian to vary continuously from an initial value H_0 at time t_0 to a certain final value H_1 at t_1 . Defining

$$T = t_1 - t_0 \quad s = (t - t_0)/T \quad (3.1)$$

and denoting by $H(s)$ the value taken by the Hamiltonian at time $t = t_0 + sT$, $H(s)$ is a continuous function of s and the following two equations hold:

$$H(0) = H_0 \quad H(1) = H_1. \quad (3.2)$$

The evolution of the system depends only on the parameter T . Thus, we can write the operator $U(t, t_0)$ describing the evolution in time of the dynamical states of the system in the *Schrödinger representation* in function of the latter parameter: recalling that $U(t, t_0)$ is completely determined once the Hamiltonian $H(t)$ of the system is given by the integral equation

$$U(t, t_0) = 1 - i\hbar^{-1} \int_{t_0}^t H(\tau)U(\tau, t_0)d\tau, \quad (3.3)$$

it is convenient to put

$$U(t, t_0) = U_T(s). \quad (3.4)$$

We are interested in determining $U(t_1, t_0) = U_T(1)$ and in studying its dependence on T . In the first limiting case we find that, *In the limit $T \rightarrow 0$, i.e. in the case of an infinitely rapid passage, the dynamical state of the system remains unchanged:*

$$\lim_{T \rightarrow 0} U_T(1) = 1. \quad (3.5)$$

Proof. Result (3.5) follows immediately from Eq. (3.5), which in the new notation reads

$$U(t, t_0) = 1 - i\hbar^{-1} \int_{t_0}^t H(s)U_T(s)ds. \quad (3.6)$$

In the limit when $T \rightarrow 0$ the second term on the right goes to zero and (3.5) is obtained.

If T is sufficiently small, we can consider in first approximation $U_T \simeq 1$. This is called the *sudden approximation*. Defining $|0\rangle$ the state wave-function at t_0 , the sudden approximation writes

$$U(t_1, t_0)|0\rangle \simeq |0\rangle. \quad (3.7)$$

Approximation (3.7) is as better as the probability ω of finding the system in a state other than the initial state at time t_1 is smaller. This probability can be written as

$$\omega = \langle 0|U^\dagger(t_1, t_0)Q_0U(t_1, t_0)|0\rangle, \quad (3.8)$$

where $Q_0 = 1 - |0\rangle\langle 0|$ is the projector onto the space of the vectors orthogonal to $|0\rangle$. Using perturbation methods on (3.3) and writing

$$\bar{H} = \int_0^1 H(s)ds = \frac{1}{T} \int_{t_0}^{t_1} H dt, \quad (3.9)$$

we then have

$$\omega = \frac{T^2}{\hbar^2} \langle 0|\bar{H}Q_0\bar{H}|0\rangle + O(T^3). \quad (3.10)$$

Finally, we can write the relation

$$\langle 0|\bar{H}Q_0\bar{H}|0\rangle = \langle 0|\bar{H}^2|0\rangle - \langle 0|\bar{H}|0\rangle^2 = (\Delta\bar{H})^2, \quad (3.11)$$

where $\Delta\bar{H}$ is the root mean square deviation of \bar{H} in the state $|0\rangle$, which yields

$$\omega = \frac{T^2(\Delta\bar{H})^2}{\hbar^2} + O(T^3). \quad (3.12)$$

From Eq. (3.12), the condition for the validity of the sudden approximation, $\omega \ll 1$, requires that

$$T \ll \hbar/\Delta\bar{H}, \quad (3.13)$$

which is simply a particular form of the time-energy uncertainty relation.

Let us now consider the other extreme case, that of a very slow modification of the Hamiltonian. In this case we have that *In the limit when $T \rightarrow \infty$, i.e. in the case of an infinitely slow, or adiabatic passage, if the system is initially in an eigenstate of H_0 it will, at time t_1 , have passed into the eigenstate of H_1 , that derives from it by continuity.* This result is known as the *adiabatic theorem*.

before proving the theorem, let us restate it in a more exhaustive way, making some assumptions:

1. the spectrum of H is entirely discrete, denoting its eigenvalues by $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_j, \dots$, and the respective projectors $P_1, P_2, \dots, P_j, \dots$, all these quantities are taken to be continuous functions of s .
2. the eigenvalues remain distinct for each s that satisfies $0 < s < 1$:

$$\varepsilon_j(s) \neq \varepsilon_k(s) \quad \forall j, k; \quad j \neq k. \quad (3.14)$$

3. the derivatives $dP_j/ds, d^2P_j/ds^2$ are well defined and piece-wise continuous in the studied interval.

As for the case seen previously, the evolution operator satisfies the Schrödinger equation

$$i\hbar \frac{d}{ds} U_T(s) = TH(s)U_T(s), \quad (3.15)$$

the Hamiltonian $H(s)$ been given by the expression

$$H(s) = \sum_j \varepsilon_j(s) P_j(s). \quad (3.16)$$

Using the former assumptions, the adiabatic theorem can be restated in terms of the evolution operator:

The evolution operator $U_T(s)$ has the asymptotic property

$$\lim_{T \rightarrow \infty} U_T(s) P_j(s) = P_j(s) \lim_{T \rightarrow \infty} U_T(s), \quad j = 1, 2, \dots \quad (3.17)$$

Proof. Let us consider first the simple case in which the subspace of each eigenvalue of $H(s)$ remains unchanged

$$P_j(s) = P_j(0) = P_j, \quad j = 1, 2, \dots \quad (3.18)$$

In this case $H(s)$ takes the simple form

$$H(s) = \sum_j \varepsilon_j(s) P_j \quad (3.19)$$

and each P_j is a constant of the motion:

$$U_T(s)P_jU_T^\dagger(s) = P_j. \quad (3.20)$$

Result (3.23) is verified for any T , thus it obviously holds for $T \rightarrow \infty$. Moreover, it is easy to see that, in this particular case, Eq. (3.15) is exactly integrable and if at time t_0 the state vector is an eigenvector of H_0 corresponding to the eigenvalue $\varepsilon_j(0)$, at time t_1 it differs from this only by a phase factor $E^{-iT\varphi_j(1)/\hbar}$, where we defined

$$\varphi_j(s) = \int_0^s \varepsilon_j(\sigma) d\sigma. \quad (3.21)$$

In the general case the eigenvectors will rotate in the Hilbert space and the exact integration of (3.15) is no longer possible. Thus, for treating these systems, is more convenient to use an appropriate change of “representation”, which will allow to eliminate this rotational motion as far as possible. The new representation is referred to as *rotating axis representation* [21]. The idea behind it is to define an unitary operator $A(s)$ and an hermitian operator $K(s)$ having the properties

$$P_j(s) = A(s)P_j(0)A^\dagger(s), \quad A(0) = 1, \quad (3.22)$$

$$i\hbar \frac{dA}{ds} = K(s)A(s). \quad (3.23)$$

For (3.21) to hold, $K(s)$ must obey the commutation relation

$$[K(s), P_j(s)] = i\hbar \frac{dP_j}{ds}, \quad (3.24)$$

and, for removing some arbitrariness in the definition of $K(s)$, is convenient to impose the condition

$$P_j(s)K(s)P_j(s) = 0, \quad (3.25)$$

which gives

$$K(s) = i\hbar \sum_j \frac{dP_j}{ds} P_j(s). \quad (3.26)$$

In the new representation the observables $H(s)$ and $K(s)$ transforms respectively into

$$H^{(A)}(s) = A^\dagger(s)H(s)A(s), \quad (3.27)$$

giving

$$H^{(A)} = \sum_j \varepsilon_j(s)P_j(0), \quad (3.28)$$

and

$$K^{(A)}(s) = A^\dagger(s)K(s)A(s). \quad (3.29)$$

Thus, the evolution operator, which reads

$$U^{(A)}(s) \equiv A^\dagger(s)U_T(s), \quad (3.30)$$

satisfies the equations

$$i\hbar \frac{dU^{(A)}}{ds} = [TH^{(A)}(s) - K^{(A)}(s)]U^{(A)}(s) \quad (3.31)$$

$$U^{(A)}(0) = 1. \quad (3.32)$$

From (3.31), for proving the theorem is sufficient to show that, in the limit when $T \rightarrow \infty$, in the term on the right of the equation $K^{(A)}(s)$ is negligible with respect to $TH^{(A)}(s)$. In fact, if this is the case, Eq. (3.31) is reduced to the initial trivial case and we are left with the following Schrödinger equation,

$$i\hbar \frac{d\phi_T}{ds} = TH^{(A)}(s)\phi_T(s) \quad (3.33)$$

$$\phi_T(0) = 1, \quad (3.34)$$

where ϕ_T is defined as the solution of Eq. (3.31), and takes the form

$$\phi_T(s) = \sum_j e^{-iT\varphi_j(s)/\hbar} P_j(0), \quad (3.35)$$

where $\varphi_j(s)$ is the one defined in (3.21). Thus, in the new representation,

$$\lim_{T \rightarrow \infty} U_T(s) = A(s)\phi_T(s). \quad (3.36)$$

To prove this result is convenient to effect a new unitary transformation [21]

$$W \equiv \phi_T^\dagger U^{(A)} = \phi_T^\dagger A^\dagger U_T, \quad (3.37)$$

whose integral form reads

$$W(s) = 1 + \frac{i}{\hbar} \int_0^s \bar{K}(\sigma) d\sigma, \quad (3.38)$$

and where

$$\bar{K}(s) \equiv \phi_T^\dagger(s) K^{(A)}(s) \phi_T(s) = \phi_T^\dagger A^\dagger K A \phi_T. \quad (3.39)$$

Defining the operator

$$F(s) \equiv \int_0^s \bar{K}(\sigma) d\sigma, \quad (3.40)$$

and considering the initial hypothesis, it is possible to demonstrate that, when $T \rightarrow \infty$,

$$F(s) = O\left(\frac{1}{T}\right) \quad (3.41)$$

and, integrating by part, that

$$W(s) = 1 + \frac{i}{\hbar} \left(F(s)W(s) - i\hbar^{-1} \int_0^s F(\sigma) \bar{K}W(\sigma) d\sigma \right). \quad (3.42)$$

In the limit $T \rightarrow \infty$, Eq. (3.42) can be rewritten as

$$W = 1 + O\left(\frac{1}{T}\right). \quad (3.43)$$

Thus, substituting (3.43) in the definition (3.37), one finally obtains

$$\lim_{T \rightarrow \infty} U_T(s) = A(s) \phi_T(s) \left[1 + O\left(\frac{1}{T}\right) \right], \quad (3.44)$$

which completes the proof of (3.36).

With the results of the adiabatic theorem in hand, we can define the so-called *adiabatic approximation*, which consists in replacing the evolution operator $U_T(1)$ by its asymptotic form

$$U(t_1, t_0) \equiv U_T(1) \simeq A(1) \phi_T(1). \quad (3.45)$$

This can be done when the rotation of the basis vectors of $H(t)$ is sufficiently slow. But, how slow is “sufficiently” slow? We would want to define a condition for which using (3.45) instead of the exact evolution operator, proves to be a good approximation, as we did in the limiting case of the sudden approximation. Actually, it can be proved that, following a treatment analogous to the calculation of ω in the latter approximation, the condition $\eta \ll 1$, where η is the probability of finding the system at time t_1 in a state different to $A(1)\phi_T(1)|0\rangle$, becomes

$$\Delta F \ll \hbar, \quad (3.46)$$

where ΔF is the root-mean-square-deviation of the observable F in the state $|0\rangle$ [21]. Unfortunately, (3.46) is not as good as (3.13) for determining the regime in which the approximation is valid. In fact, the observable F is much more difficult to construct than the observable \bar{H} involved in (3.13). For obtaining a better condition, it is possible to restate (3.46) in terms of more accessible quantities:

$$\left| \frac{\alpha_t^{\max}}{\omega_t^{\min}} \right| \ll 1, \quad (3.47)$$

where, denoting the set of basis vectors of $H(t)$ as

$$|j\rangle_t = A(t)|j\rangle_0 \quad (3.48)$$

$$H(t)|j\rangle_t = \varepsilon_j(t)|j\rangle_t, \quad (3.49)$$

α_t^{\max} and ω_t^{\min} are respectively the maximum angular velocity of the eigenvector $|i\rangle_t$ and the minimum Bohr frequency for the transition from i to its nearest neighbor

$$\omega_t^{\min} = \min_{i,j} \omega_{i,j}(t) = \min_{i,j} |\varepsilon_j(t) - \varepsilon_i(t)| / \hbar. \quad (3.50)$$

3.2 Adiabatic approximate functional for TDDFT

We have shown in the first chapter that, while being in principle exact theories, DFT and TDDFT require approximations for the form of the unknown exchange-correlation potential (and consequently for the XC potential

energy). We have also stated that any ground state approximation (LDA, GGA, Hybrid) of the functional automatically provides an adiabatic approximation for use in TDDFT. In fact, an approximate adiabatic potential can be defined as

$$v_{XC\sigma}^{\text{ad}}[n](\mathbf{r}, t) = v_{XC\sigma}^{\text{gs}}[n_0](\mathbf{r})|_{n_{0\sigma}(\mathbf{r})=n_{\sigma}(\mathbf{r}, t)}, \quad (3.51)$$

i.e. the exchange-correlation potential (functional of the density n) at any time is simply the ground-state XC potential at that instant. As we saw previously, the approximation is as better as the slower is the perturbation. If the perturbation is sufficiently slow, the system can be seen as if it remains always in its instantaneous ground-state (consistently with Eq. (3.45)). Actually, a good aspect of the adiabatic approximation is that in many cases, even if the system considered is not in this slowly varying regime, results obtained with this approximation can be significantly accurate. The most commonly used is the one built on the ground-state local density approximation seen in chapter one, which is called adiabatic local density approximation (ALDA). It employs the functional form of the static LDA with a time-dependent density:

$$v_{XC\sigma}^{\text{ALDA}}[n](\mathbf{r}, t) = v_{XC\sigma}^{\text{ALDA}}(n_{\alpha}(\mathbf{r}, t), n_{\beta}(\mathbf{r}, t)) = \left. \frac{d\varepsilon_{XC}^{\text{unif}}}{dn_{\sigma}} \right|_{n_{\sigma}=n_{\sigma}(\mathbf{r}, t)}, \quad (3.52)$$

where $\varepsilon_{XC}^{\text{unif}}(n_{\alpha}, n_{\beta})$ is the exactly known exchange-correlation energy density of the uniform electron gas of spin densities n_{\uparrow} and n_{\downarrow} .

Chapter 4

Electronic correlation

4.1 Electron correlation and exchange

Important insight into the behaviour of interacting many-particle systems can be obtained by measurements of the correlation of the system itself. In fact, the study of the electron correlation due to the Coulomb interaction can improve the understanding of various phenomena. From a mathematical point of view, the idea of electron correlation can be simply understood considering the equation

$$\rho(\mathbf{r}_i, \mathbf{r}_j) \sim \rho(\mathbf{r}_i)\rho(\mathbf{r}_j), \quad (4.1)$$

which holds for two independent electrons i and j . Here, $\rho(\mathbf{r}_i, \mathbf{r}_j)$ represent the probability density of finding electron i at \mathbf{r}_i and electron j at \mathbf{r}_j (joint electron density). If these two electrons are correlated, Eq. (4.1) is no longer satisfied, i.e. the probability of finding one electron at a certain position depends on the position of the other electron. Thus, the product of their independent density function does not describe properly the real situation.

It is well known that within one of the most commonly used methods for studying many-body systems, the *Hartree-Fock method*, the antisymmetric wave-function is approximated by a single Slater determinant. However, exact wave-functions cannot generally be expressed in this way, due to the

Coulomb correlation, which is not taken into account in the method. In fact, the total electronic energy obtained with the Hartree-fock method is always above the exact energy computed solving the non-relativistic Schrödinger equation within the *Born-Oppenheimer approximation*. the difference between these two energies is called *correlation energy* [22]. Actually, some “correlation” is already considered within the Hartree-Fock theory in the electron exchange term, which takes into account the correlation between electrons with the same spin (for the *exchange effect*, electrons with the same quantum spin number m_s have an attractive interaction). This type of correlation is usually referred to as *Fermi correlation*. For a correct description of the system, one has to consider also the *Coulomb correlation*, which consist in the correlation between the spatial position of electrons due to their Coulomb repulsion, and the possible correlation due to the overall symmetry or total spin of the studied system.

Correlation can be divided into static and dynamical correlation, where the former is important in systems where the ground state is well described only with more than one (nearly-)degenerate determinant, and the latter consist in the correlation of the movement of electrons. For what concern the strength of the correlation, it is common to distinguish between *weakly* and *strongly* correlated systems. A system of electrons is strongly correlated when the *Fermi liquid model* of correlated electrons is not able to describe it, due to the great importance of the interactions (e.g. the Hubbard model is a typical example of a strongly-correlated system). This can be an useful classification, however, for a more quantitative treatment of the correlation, it is necessary to find ways for “measuring” the correlation strength. in the next paragraphs we will examine some different ways for measuring correlation and discuss their features.

4.2 Correlation measurements

We are interested in finding ways for getting more insight into the correlation of a system. This aim can be reached throughout the determination of some quantities which allow to obtain quantitatively information about correlation. We have seen that electron correlation is naturally defined by the difference between the energy computed from the exact non-relativistic Schrödinger equation and the approximate one obtained within the Hartree-Fock method. This difference is the correlation energy. In spite of its straightforward definition, correlation energy is not usually the best quantity for studying correlation. Often is preferable to consider other quantities, as *correlation functions* and *entanglement entropy*.

4.2.1 Pair correlation function

Correlation functions are a group of functions that allow to measure directly the correlation of a system. Especially useful are the strictly related *exchange-correlation hole function* $\rho_{xc}(\mathbf{r}_1, \mathbf{r}_2)$ and the *pair-correlation function* $g_\sigma(\mathbf{r}_1, \mathbf{r}_2)$. Defining the former is somehow simpler, but the latter is easier to compute and interpret. Their definition comes from the definition of the function

$$P_{\sigma_1\sigma_2}(\mathbf{r}_2|\mathbf{r}_1) = \frac{\Gamma_{\sigma_1,\sigma_2}(\mathbf{r}_2, \mathbf{r}_1)}{\rho_{\sigma_1}(\mathbf{r}_1)} \quad (4.2)$$

Here, $\Gamma_{\sigma_1\sigma_2}(\mathbf{r}_2|\mathbf{r}_1)$ is the diagonal two-particle density matrix

$$\begin{aligned} \Gamma_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') &= \langle \psi | \widehat{\Psi}_\sigma^+(\mathbf{r}) \widehat{\Psi}_{\sigma'}^+(\mathbf{r}') \widehat{\Psi}_{\sigma'}(\mathbf{r}') \widehat{\Psi}_\sigma(\mathbf{r}) | \psi \rangle \\ &= N(N-1) \int |\psi(\mathbf{r}\sigma, \mathbf{r}'\sigma', x_3 \cdots x_N)|^2 dx_3 \cdots dx_N, \end{aligned} \quad (4.3)$$

where $x_i = (\sigma_i, \mathbf{r}_i)$ and $\rho_{\sigma_1}(\mathbf{r}_1)$ is the electron density for electrons in \mathbf{r}_1 with spin σ_1 . The function $P_{\sigma_1\sigma_2}(\mathbf{r}_2|\mathbf{r}_1)$ gives the probability of finding an electron with spin σ_2 in \mathbf{r}_2 if one knows that there is an electron with spin σ_1 in \mathbf{r}_1 . The exchange-correlation hole function $\rho_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)$ is defined by the equation

$$P_{\sigma_1\sigma_2}(\mathbf{r}_2|\mathbf{r}_1) = \rho_{\sigma_2}(\mathbf{r}_2) + \rho_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2). \quad (4.4)$$

The function ρ_{xc} represents a hole in the electron density $\rho_\sigma(\mathbf{r}_2)$, so that

$$\sum_{\sigma_2} \int \rho_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = -1. \quad (4.5)$$

The electron repulsion energy between the electrons is

$$\langle \psi | \widehat{W} | \psi \rangle = \frac{1}{2} \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + W_{xc}, \quad (4.6)$$

where the exchange correlation energy W_{xc} is given by

$$\begin{aligned} W_{xc} &= \frac{1}{2} \sum_{\sigma_1\sigma_2} \int \frac{\rho_{\sigma_1}(\mathbf{r}_1)\rho_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{1}{2} \sum_{\sigma_1} \int \rho_{\sigma_1}(\mathbf{r}_1) v_{xc,\sigma_1}^h(\mathbf{r}_1) d\mathbf{r}_1 \end{aligned} \quad (4.7)$$

and $v_{xc,\sigma_1}^h(\mathbf{r}_1)$ is the potential of the exchange-correlation hole of the reference electron at \mathbf{r}_1 defined as

$$v_{xc,\sigma_1}^h(\mathbf{r}_1) = \sum_{\sigma_2} \int \frac{\rho_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (4.8)$$

The probability of finding an electron near the reference one is reduced due to two effects: the Pauli principle and the Coulomb repulsion. The hole function corresponding to the first effect is called the exchange-hole function, and is easily calculated from the Slater determinant (the wave function for such a system). For systems of interacting electrons the exchange-correlation function is more difficult to calculate, but it can be shown to be

$$v_{xc,\sigma_1}^h(\mathbf{r}_1) = \sum_{\sigma_2} \int_0^\infty 4\pi s^2 \frac{\overline{\rho}_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, s)}{s} ds, \quad (4.9)$$

where

$$\overline{\rho}_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, s) = \int \rho_{xc}^{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_1 + \mathbf{s}) \quad (4.10)$$

is the spherical average part of the exchange-correlation hole. In a similar way of the one followed for defining the exchange-correlation hole, is possible to define the pair-correlation function

$$g_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{\Gamma_{\sigma_1\sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{\rho_{\sigma_1}(\mathbf{r}_1)\rho_{\sigma_2}(\mathbf{r}_2)}, \quad (4.11)$$

from which is possible to rewrite the electron-repulsion energy

$$\langle \psi | \widehat{W} | \psi \rangle = \frac{1}{2} \sum_{\sigma_1 \sigma_2} \rho_{\sigma_1}(\mathbf{r}_1) \rho_{\sigma_2}(\mathbf{r}_2) \frac{g_{\sigma_1 \sigma_2}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (4.12)$$

Note that the r_{12}^{-1} potential is replaced by the screened potential g/r_{12} due to exchange and correlation effects. In terms of g , the expression for the exchange-correlation energy becomes

$$W_{xc} = \frac{1}{2} \sum_{\sigma_1 \sigma_2} \int \rho_{\sigma_1}(\mathbf{r}_1) \rho_{\sigma_2}(\mathbf{r}_2) \frac{g_{\sigma_1 \sigma_2}(\mathbf{r}_1, \mathbf{r}_2) - 1}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (4.13)$$

4.2.2 Correlation energy and Entanglement Entropy

We know that one of the most direct source of information about correlation is the correlation energy. Considering a system in its ground state, the total energy can be written from a Kohn-Sham formalism as

$$E = \int n v_{ext} + T_S[n] + E_H + E_{xc}, \quad (4.14)$$

where n is the electron density and v_{ext} is the external potential applied to the chain. $T_S[n]$ is the kinetic energy of a non interacting electrons system and E_H is the ‘‘Hartree-like’’ term. The last term is the exchange correlation energy

$$E_{xc} = E_x + E_c \quad (4.15)$$

where the first term is the H-F exchange energy and the second one is the energy due to correlation effects (correlation energy). E_c can be evaluated considering the minimal principle

$$\langle \psi | \widehat{H}_{exact} | \psi \rangle \geq E_0. \quad (4.16)$$

Correlation energy is not as useful for describing correlation strength in dynamical systems. For such systems other quantum-kinematic measures of the correlation strength have to be used. Moreover, correlation energy provides information about the *total* correlation of the system only. In this thesis work we are interested in the correlation between two electrons in

particular sites (within the Hubbard model) and not on the correlation of the whole system. Thus, we discharged correlation energy in favour of the pair correlation function.

Another way of measuring the correlation of a system is to consider the so-called ‘‘Von Neumann Entanglement Entropy’’. The general definition of entanglement is related to the definition of separability: considering a physical system C consisting in two subsystems A and B , for the partition of the system in A and B , the state $|\psi\rangle_C$ is defined *separable* if it is possible to write

$$|\psi\rangle_C = |\psi\rangle_A \otimes |\psi\rangle_B \quad (4.17)$$

otherwise, is defined inseparable or *entangled* (separability depends on the partition considered). The Von Neumann entropy can be seen as the quantum version of the classical Shannon entropy (is related to Shannon’s measure of information, which is important in the context of information capacity) and is related to Gibbs’s entropy from statistical mechanics. The practical definition of entanglement entropy is based on the concept of *reduced density matrix*. A density matrix is a positive matrix that describes the state of an ensemble (a large number of copies of the same quantum system). It takes the general form

$$\rho = \sum_i c_i |\psi_i\rangle \langle \psi_i|, \quad (4.18)$$

where c_i is the portion of the ensemble whose states are ψ_i . The formalism based on density matrices is necessary whenever the system studied is not completely isolated. If we consider a system C divided into two subsystems A and B each with an Hilbert space H_A and H_B , the state of the composite system is $\Psi \in H_A \otimes H_B$. In this case, the state of A cannot be in general described by a unit vector in the proper Hilbert space, but is necessary to use the density matrix formalism. The density matrix which describes the state is

$$\rho_A \equiv \sum_j \langle j|_B (|\Psi\rangle \langle \Psi|) |j\rangle_B = Tr_B \rho_T, \quad (4.19)$$

where $\rho_T = |\Psi\rangle \langle \Psi|$ is the projection operator onto the state $|\Psi\rangle$. ρ_A is usually

called reduced density matrix. The definition of the von Neumann entropy follows directly from the Shannon entropy from classical information theory:

$$S(\rho) = -\text{Tr}(\rho \log_2 \rho). \quad (4.20)$$

Note that the mixed state ρ takes the place of the classical probability distribution (in fact, ρ is essentially a probability distribution over an ensemble).

As for the correlation energy, the entanglement entropy is not really suitable for our purposes. For using (4.20), we need to define properly the partition of the system. Considering that we are interested in electron correlation, the most natural way for making the partitions is to consider a subsystem composed by a single electron, and another subsystem consisting in all the other electrons. Within the Hubbard model, in this way we can for example study the correlation between an electron in a certain site and all the other electrons, but we will not be able to obtain information about the correlation between only two electrons.

Chapter 5

Computational aspects

5.1 Time dependence and Crank-Nicolson algorithm

The time dependence of a quantum system described by the wave-function ψ is defined by the well known time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{x}, t) = \hat{H} \psi(\mathbf{x}, t). \quad (5.1)$$

Equation (5.1) holds for any wave-function (i.e. not necessarily for eigenfunctions of \hat{H}), but the form of the solutions varies with the properties of the wave-function and the Hamiltonian. Essentially, it is possible to distinguish between three cases:

1. The Hamiltonian \hat{H} is independent of t and the wave-function at the initial time $\psi(t = 0)$ is an eigenfunction of \hat{H} .
2. \hat{H} is independent of t , but $\psi(t = 0)$ is not necessarily an eigenfunction of the Hamiltonian.
3. \hat{H} is time-dependent

In the first case solutions are simply of the form

$$\psi(\mathbf{x}, t) = \psi(\mathbf{x}, 0) e^{-iEt/\hbar} \quad (5.2)$$

where $\hat{H}\psi = E\psi$ at $t = 0$. The wave-functions change in the most trivial way and the solutions are defined *stationary states*. This name follows from the observation that any physical observable is stationary: considering the generic operator \hat{O} , its expectation value satisfies the equation

$$\langle \hat{O} \rangle \Big|_t = \int \psi^*(\mathbf{x}, t) \hat{O} \psi(\mathbf{x}, t) d\mathbf{x} \quad (5.3)$$

$$= \int \psi^*(\mathbf{x}, t=0) e^{iEt/\hbar} \hat{O} \psi(\mathbf{x}, t=0) e^{-iEt/\hbar} d\mathbf{x} \quad (5.4)$$

$$= \langle \hat{O} \rangle \Big|_{t=0} \quad (5.5)$$

where we considered that $e^{-iEt/\hbar}$ is a constant, so it can be moved (linear operators) and cancelled with the other exponential term. If the system is not initially prepared in an eigenstate of the time-independent Hamiltonian, it is necessary to solve the differential equation considering the property of completeness, for which $\psi(t=0)$ can always be expressed as a linear combination of eigenfunctions of \hat{H} :

$$\psi(t=0) = \sum_j c_j \phi_j(\mathbf{x}), \quad (5.6)$$

where $\hat{H}\phi_j = E_j\phi_j$. Thus, the solution is

$$\psi(\mathbf{x}, t) = \sum_j c_j \phi_j(\mathbf{x}) e^{-iE_j t/\hbar}, \quad (5.7)$$

i.e. each eigenfunctions that contributes to $\psi(t=0)$ oscillate at its own rate. In the most general case in which the Hamiltonian \hat{H} is time-dependent, it is not possible to find analytic solutions and numerical techniques are needed. Actually, analytic progress is only possible when the time dependence of the Hamiltonian is weak. In this case, solutions to the time-dependent Schrödinger equation follows from *time-dependent perturbation theory*:

$$\psi(\mathbf{x}, t) = \sum_j c_j(t) \phi_j(\mathbf{x}) e^{-iE_j t/\hbar}, \quad (5.8)$$

considering $\hat{H}(\mathbf{x}, t) = \hat{H}_0(\mathbf{x}) + \Delta\hat{H}(\mathbf{x}, t)$ and $\hat{H}_0\phi_j = E_j\phi_j$. The time dependence of the coefficients c_j is determined by the equations of motion

$$\dot{c}_k(t) = \frac{1}{i\hbar} \sum_j c_j(t) e^{-i(E_j - E_k)t/\hbar} \Delta H_{kj}(t), \quad (5.9)$$

where $\Delta H_{kj}(t) = \int \phi_k^*(\mathbf{x}) \Delta \hat{H}(\mathbf{x}, t) \phi_j(\mathbf{x}) dx^3$.

Proof. Equation (5.8) follows directly from (5.1), considering that for weak $\Delta \hat{H}(t)$, the function $c_j(t)$ will be a slowly varying. From here, using the time-dependent Schrödinger equation:

$$\begin{aligned} i\hbar \sum_j \left\{ \dot{c}_j(t) e^{-iE_j t/\hbar} \phi_j + c_j \left(\frac{-iE_j}{\hbar} \right) e^{-iE_j t/\hbar} \right\} \\ = \sum_j \left\{ c_j e^{-iE_j t/\hbar} E_j \phi_j + c_j e^{-iE_j t/\hbar} \Delta \hat{H}(\mathbf{x}, t) \phi_j(\mathbf{x}) \right\}, \end{aligned} \quad (5.10)$$

and, deleting the two equal terms on the right and on the left part of the equation,

$$i\hbar \sum_j \dot{c}_j(t) e^{-iE_j t/\hbar} \phi_j = \sum_j c_j e^{-iE_j t/\hbar} \Delta \hat{H}(\mathbf{x}, t) \phi_j(\mathbf{x}). \quad (5.11)$$

Equation (5.9) is obtained applying the operator $\hat{O}\varphi = \phi_k^* \int \varphi d\tau$ to both sides of the previous equation and considering $\int \phi_k^* \phi_j dx^3 = \delta_{kj}$.

Equation (5.9) have to be solved iteratively, starting from the known initial values of the functions $c_1(t), c_2(t), \dots$. If one considers the case where $\psi = \phi_s$ at $t = 0$ (i.e. $c_j = 0 \forall j \neq s, c_s = 1$ at $t = 0$), the simpler expression for the coefficients is found,

$$c_k(t) = \frac{1}{i\hbar} \int_{t'=0}^t e^{-i\omega_{sk}t'} \Delta H_{ks}(t') dt', \quad (5.12)$$

where the notation $(E_s - E_k)/\hbar = \omega_{sk}$ is used. The theory presented here is the first-order time-dependent perturbation theory. It is valid provided that c_k does not increase too much from zero, i.e. c_s does not decline too much from unity. Obviously, it is possible to consider terms of higher order in the expansion of $\hat{H}(\mathbf{x}, t)$ for higher order theories.

As stated in the former paragraph, the time-dependent Schrödinger equation has usually non-trivial or, in the most general case, any analytic solution. Moreover, if a many-body system is considered, even if in the case of time-independent Hamiltonian, analytic solutions are not practical. For these reasons, numerical approaches which do not require the direct solution of the differential equation are more efficient. The *Crank-Nicolson Method* [23] is a useful method for the integration of the time-dependent Schrödinger equation for the complex valued wave function. One of the most appealing features of this method is his numerical stability. The C-N method moves essentially from the so called “explicit crude euler method”: considering the time-dependent Schrödinger equation (5.1), the time evolution operator $\widehat{U}(\Delta t) = e^{i\Delta t\widehat{H}}$ has the property $\psi^n = \widehat{U}^n(\Delta t)\psi^0$, where $\psi^n = \psi_{t=n\Delta t}$ (note that the former equations actually hold only for the case of a time-independent Hamiltonian, while the Crank-Nicolson method has a more general validity). The method is simply based on the expansion of $e^{-i\Delta t\widehat{H}}$ into a Taylor series where only the leading terms are kept. Thus

$$\psi^{n+1} = (1 - i\Delta t\widehat{H})\psi^n. \quad (5.13)$$

In the Matrix formalism, Eq. (5.13) can be written as

$$\psi^{n+1} = \mathbf{A} \cdot \psi^n \quad (5.14)$$

where the matrix \mathbf{A} is deducible from the matrix representation of \widehat{H} and from Eq. (5.13). This scheme is also called the one step forward method. It is an explicit scheme as the wave function value is evaluated at any time step in terms of the known values of the wave function at past time without the need to solve a system of differential equations. The Crude Euler method however has proved to be inefficient for integrating the Schrödinger equation. The main problem of this scheme is its numerical instability caused by the fact that the Eq. (5.13) is not centred [24]. The Crank Nicholson scheme for the Schrödinger equation is based on the reformulation of the previous equation with the aim to obtain a more centred equation. Eliminating ψ^n between the

two Equations

$$\psi^{n+1} = e^{-i\Delta t \hat{H}} \psi^n, \quad \psi^{n-1} = e^{i\Delta t \hat{H}} \psi^n, \quad (5.15)$$

the identity

$$e^{i\Delta t \hat{H}} \psi^{n+1} = e^{-i\Delta t \hat{H}} \psi^{n-1} \quad (5.16)$$

is obtained, or similarly

$$e^{i\hat{H}\Delta t/2} \psi^{n+1} = e^{-i\hat{H}\Delta t/2} \psi^n. \quad (5.17)$$

As for the Crude Euler scheme, Eq. (5.17) reads

$$\mathbf{A} \cdot \psi^{n+1} = \mathbf{B} \cdot \psi^n, \quad (5.18)$$

where

$$\mathbf{A} = (\mathbf{I} + i\mathbf{H} \frac{\Delta t}{2}), \quad \mathbf{B} = (\mathbf{I} - i\mathbf{H} \frac{\Delta t}{2}). \quad (5.19)$$

The scheme in Eq. (5.19) is an implicit one because the matrix \mathbf{A} need to be inverted in order to compute ψ^{n+1} . On replacing \hat{H} by its finite difference approximation in \mathbf{x} , we have a complex tridiagonal system to solve. The method is stable, unitary, and second-order accurate in space and time (stability analysis based on the Courant-Levi-Fredrichs criterion shows that in the C-N scheme the error do not grows exponentially as in the Crude Euler scheme [24]). Note that the unitary of the algorithm is especially useful for quantum mechanics, where unitarity assures that the normalization of the wavefunction is unchanged over time.

5.2 Optimization algorithms and Powell's method

Optimization is the name used for a very large field of numerical research which deals with methods for, given a function f of one or more independent variables, finding the value of those variables for which f takes on a maximum or a minimum value. Maximization and minimization are trivially related to each other. In fact is always possible to redefine a second function f' for which is satisfied the equation $f' = -f$. From a computational point of

view, a good optimization algorithm should have three main characteristics: it should be quick, cheap and able to work in small memory. It is possible to distinguish between two mayor types of optimization algorithms which are global and local optimization algorithms. The first group is concerned in finding *global* extrema (minimum or maximum points), while the second handles *local* extrema (the highest or lowest in a finite neighbourhood and not on the boundary of that neighbourhood). Finding a global minimum is not usually an easy task. If the searched extremum is known to be in a certain range of values is always better to use local optimization (e.g. in ground-state searching related problems is more practical to use local optimization, provided that one knows approximately where the value of interest should be).

In this chapter we will focus on local optimization, and in particular on *Powell's method*. The latter is the prototype of a class of algorithms called *direction set methods*. Powell's method is a multi-dimensional optimization algorithm, which requires a one-dimensional minimization subalgorithm such as *Brent's method* and does not need to compute the gradient of the function. For what concern memory usage, being N the number of dimensions, this method requires storage of order N only (unlike other multi-dimensional algorithms, as for example the *simplex downhill method*, which requires a storage of order N^2).

Before moving to multi-dimensional minimization, let us talk briefly about one-dimensional minimization. We will from now on consider optimization as a minimization process. The search for a local minimum in one dimension starts with the *bracketing* (actually, there are some one-dimensional algorithms that do not require a rigorous initial bracketing, but they are usually not reliable as the ones which requires it). A minimum is known to be bracketed only when there is a triplet of points, $a < b < c$ (or $c < b < a$), such that $f(b)$ is less than both $f(a)$ and $f(c)$. Defined the first triplet of points, the algorithm will step downhill redefining at each step a new set of points until the bracketing interval (a, c) is acceptably small. This is done by choos-

ing at each step a new point x between a and b or between b and c . If for example we make the latter choice, the algorithm will evaluate $f(x)$, then, if $f(x) > f(b)$, the new triplet will be (a, b, x) . contrariwise, if $f(x) < f(b)$, the chosen triplet will be (b, x, c) (i.e. the middle point of the new triplet is always the abscissa whose ordinate is the best minimum achieved so far). Now, we still have to answer two questions: we said that the algorithm will keep choosing new middle points until the bracketing interval is tolerably small. but, how small can be this interval? and for what concern the choice of the middle point, which is the best way for defining the new triplet? The answer to the first question follows considering the second order expansion of the function f evaluated on an extremum point x ,

$$f(x) = f(b) + \frac{1}{2}f''(x)(x - b)^2. \quad (5.20)$$

From here it is easy to see that it is not possible to bracket a minimum in the interval $((1 - \epsilon)b, (1 + \epsilon)b)$ where ϵ is the computer floating point precision (10^{-16} for floating point numbers in double precision). In fact, the second term on the right in (5.20) is negligible whenever

$$|x - b| < \sqrt{\epsilon}|b| \sqrt{\frac{2|f(b)|}{b^2 f''(b)}}. \quad (5.21)$$

For most functions, the final square root is a number of order unity. Therefore, it is hopeless to ask for a bracketing interval of width less than $\sqrt{\epsilon}$ -times its central value (minimum-finding routines usually requires an user-supplied argument named *tol* and return with an abscissa whose fractional precision is about $\pm \mathbf{tol}$). For what concern the choice of the bracketing triplet, there are different strategies for choosing the new point x given (a, b, c) . It is possible to show that, for handling the worst possible case of function minimization, the optimal bracketing interval has its middle point b a fractional distance from one end and the other equal to those of the *golden mean* or *golden section* (i.e. a fractional distance 0.38197 from one end (say a), and 0.61803 from the other end (say b)). Thus, the strategy at each step is, given the initial triplet, to chose the next point in the larger of the two intervals with

the previous fractional distances. Even if the initial triplet does not satisfy the golden ratios, the procedure of choosing successive points at the golden mean point of the larger segment will quickly converge you to the proper self-replicating ratios. The algorithm based on this strategy is called *golden section search*. If the function to be minimized is nicely parabolic near its minimum, the *parabolic interpolation method* can be used instead of the golden section search. Given a sufficiently smooth function, the parabola fitted through any three points allows to jump in a single leap to the minimum, or at least very near to it. Actually, algorithm based only on parabolic interpolation are not practical (for example they are not able to distinguish between maxima and minima). Brent's method combines the good aspects of the golden section search with the faster parabolic interpolation, allowing to switch between the two schemes at the occasion, keeping track at each step of six function points.

Using a routine for line minimization as Brent's method, the simplest method for general multidimensional minimization is simply obtained: one defines a set of unit vectors $\mathbf{e}_0, \mathbf{e}_1, \dots, \mathbf{e}_{N-1}$ (*set of directions*). then, using the line minimization routine, moves along the first direction to its minimum, then from there along the second direction to its minimum, and so on, cycling through the whole set of directions as many times as necessary, until the function stops decreasing. This simple method, while being able to find minima for a large range of different types of functions, it is not the most efficient and reliable one. Its main problem hides in the definition of the set of directions: If the set of vectors is not chosen wisely, the minimization along one direction can be spoiled by the subsequent minimization along another one, causing an interminable cycling through the set of directions. In general, in N dimensions, if the function's second derivatives are much larger in magnitude in some directions than in others, then many cycles through all N basis vectors will be required in order to get anywhere. *Direction set methods* are those general multidimensional minimization algorithms which provide prescriptions for updating the set of directions as the method proceeds, with

the aim of obtaining a set which includes some very good directions that allow to go far along narrow valleys or some non-interfering directions with the property that minimization along one of them will not spoil the minimization along the previous ones. Directions sets which satisfies the latter property are usually defined *conjugate directions*. Two vectors \mathbf{u} and \mathbf{v} are conjugate if they satisfy the equation

$$\mathbf{u} \cdot \mathbf{A} \cdot \mathbf{v} = 0, \quad (5.22)$$

where \mathbf{A} is the Hessian matrix of the function f . Equation (5.22) follows from the observation that, taken some point \mathbf{P} as the origin of the coordinate system with coordinate \mathbf{x} , any function f can be expanded to the second order as

$$f(x) = f(\mathbf{P}) + \sum_i \frac{\partial f}{\partial x_i} x_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 f}{\partial x_i \partial x_j} x_i x_j + \dots \quad (5.23)$$

$$\approx c - \mathbf{b} \cdot \mathbf{x} + \frac{1}{2} \mathbf{x} \cdot \mathbf{A} \cdot \mathbf{x}, \quad (5.24)$$

where

$$c \equiv f(\mathbf{P}), \quad \mathbf{b} \equiv -\nabla f|_{\mathbf{P}}, \quad [\mathbf{A}]_{ij} \equiv \left. \frac{\partial^2 f}{\partial x_i \partial x_j} \right|_{\mathbf{P}}. \quad (5.25)$$

From Eq. (5.23), the gradient of the function ∇f , which is calculated as

$$\nabla f = \mathbf{A} \cdot \mathbf{x} - \mathbf{b}, \quad (5.26)$$

changes while moving along one direction as

$$\delta(\nabla f) = \mathbf{A} \cdot (\delta \mathbf{x}). \quad (5.27)$$

The condition for which the motion along a new direction \mathbf{v} does not spoil the previous optimization along \mathbf{u} is simply that the gradient remains perpendicular to \mathbf{u} . This condition is exactly (5.22).

Powell's method was the first algorithm to show a good basic procedure for producing a set of N mutually conjugate directions. Initializing the set of directions to the basis vectors, the repetition of a series of steps allows in

k iterations, for a quadratic form like (5.23), to produce a set of directions \mathbf{u}_i whose last k members are mutually conjugate. Thus, N iterations of the basic procedure (amounting to $N(N+1)$ line minimizations) exactly minimizes a quadratic form. Actually the original Powell's quadratically convergent algorithm, which required to discharge at each stage part of the information about the conjugate directions already built up, tended to produce sets of directions that become linearly dependent, giving the wrong answer. There exist several different modified Powell's method (proposed by Powell himself) that fix up the problem of linear dependence, reinitialising the set of directions in various ways, or giving up the property of quadratic convergence in favour of a scheme that tries to find some good directions along narrow valleys.

Chapter 6

Results

In order to get some insight into TDDFT functionals, our aim is to obtain the exact time-dependent Kohn-Sham potentials V_{KS} for 1D Hubbard chains, driven by a d.c. external field, using the time-dependent electron density and current density obtained from exact many-body time evolution. Obtained the the exact potential, we will compare the exact V_{xc} to two different approximate potential: an adiabatically exact $V_{\text{xc}}^{\text{ad}}$, and a potential which is essentially adiabatic with respect to the external potential and that we will call “instantaneous ground state” $V_{\text{xc}}^{\text{igs}}$. Then the effectiveness of these two approximation will be analyzed, comparing the obtained charge densities in several different cases. We are not only interested in studying adiabatic approximations. In this thesis work we are going to look also at approximations for the exchange-correlation potential V_{xc} and its gradient, based on the local density and on the local current density. In order to do this, we will use an explicit comparison between the found potentials and the local quantities, and a sort of “fitting method” that will consider at the same time the charge and the current density. Finally, we will try to get some insight into the respective roles of ground-state and excited-state correlation in the time-dependent system, as reflected in the potentials, through the pair correlation function.

6.1 Interacting system

In this work we study 1D open-ended Hubbard chains, subjected to external TD perturbing potentials. These systems are described by the Hamiltonian

$$\hat{H} = U \sum_R \hat{n}_{R\uparrow} \hat{n}_{R\downarrow} - t \sum_{\langle RR' \rangle \sigma} \hat{\Psi}_{R\sigma}^\dagger \hat{\Psi}_{R'\sigma} + \sum_{R\sigma} V_R^{\text{ext}}(\tau) \hat{n}_{R\sigma}. \quad (6.1)$$

Note that Eq. (6.1) is simply the Hubbard chain Hamiltonian (2.1), where the energy of the single electron has been omitted. This can be done without loss of generality because this energy term does not modify the physics of the system. In fact, from a matricial point of view, it is nothing more than a constant value added to the diagonal of the Hamiltonian matrix. For the rest of the equation holds what we said in Chapter 2: U is the interaction energy, t is the hopping parameter and $V_R^{\text{ext}}(\tau)$ is a local external TD field. $\langle RR' \rangle$ denotes nearest-neighbour sites and $\hat{n}_{R\sigma} = \hat{\Psi}_{R\sigma}^\dagger \hat{\Psi}_{R\sigma}$, $\sigma = +1, -1$. In the Hamiltonian we use $\hbar = 1$ and $t = 1$, thus the unit of time is \hbar/t .

Practically, Hamiltonian (6.1) is represented by a (sparse) matrix (as provided by the matrix representation of quantum mechanics). The state of the system is defined by the four possible electron configurations consistent with the Pauli exclusion principle for each ion. Thus, we consider the Hilbert space whose base consists in the Slater determinants obtained considering all the possible configurations of the system, e.g., for two sites and two electrons,

the elements of the base are

$$\frac{1}{\sqrt{2}} (\phi_L(1)\phi_L(2) \uparrow_1\downarrow_2 - \phi_L(1)\phi_L(2) \downarrow_1\uparrow_2) \quad (6.2)$$

$$\frac{1}{\sqrt{2}} (\phi_L(1)\phi_R(2) \uparrow_1\uparrow_2 - \phi_L(2)\phi_R(1) \uparrow_1\uparrow_2) \quad (6.3)$$

$$\frac{1}{\sqrt{2}} (\phi_L(1)\phi_R(2) \uparrow_1\downarrow_2 - \phi_L(2)\phi_R(1) \downarrow_1\uparrow_2) \quad (6.4)$$

$$\frac{1}{\sqrt{2}} (\phi_L(1)\phi_R(2) \downarrow_1\uparrow_2 - \phi_L(2)\phi_R(1) \uparrow_1\downarrow_2) \quad (6.5)$$

$$\frac{1}{\sqrt{2}} (\phi_L(1)\phi_R(2) \downarrow_1\downarrow_2 - \phi_L(2)\phi_R(1) \downarrow_1\downarrow_2) \quad (6.6)$$

$$\frac{1}{\sqrt{2}} (\phi_R(1)\phi_R(2) \uparrow_1\downarrow_2 - \phi_R(2)\phi_R(1) \downarrow_1\uparrow_2) \quad (6.7)$$

for a total of six Slater determinants. While for a two sites half-filled Hubbard chain the base is made up of six elements, for an eight sites half-filled Hubbard chain the base consists of 12870 elements. the dimension of the matrix increases rapidly with the number of sites and depends on the number of electrons. From combinatorics, the number of Slater determinants which cover all the possible combinations is

$$\frac{(2m!)}{(2m - N)!(N!)}, \quad (6.8)$$

where m and N are respectively the number of sites and electrons.

Since we are interested in the ground-state of the system, we can actually work with a reduced Hilbert space which consists in those state for which the S^2 operator yields zero. The reason for doing this is related to the exchange effect and the fact that high spin states has lower energy than low spin states. Thus, it is sufficient to diagonalize the reduced matrix, neglecting those low energy states. The smaller dimensions of the reduced matrix allow to reduce the computational cost of the diagonalization and of the time-propagation. However, this strategy proved to be not too efficient. In fact, the time saved using the reduced base is small compared to the computation time spent in building the S^2 matrix (which is used for passing from one base to the other) and in the back-engineering of the KS potential.

After having prepared the system in its ground state, we apply the external perturbation. The external perturbing potential $V_R^{\text{ext}}(\tau)$ decreases with constant gradient from the right-most site to the left-most site (on which its value is zero), representing a uniform d.c. electric field (note that in the Hubbard world we just have to define the potential on the N sites of the system, thus the perturbation consists of N scalar potentials). For its time-dependence we study two different cases:

1. the field is turned on at its full strength V_{max} at $\tau = 0$, remaining constant thereafter ('instantaneously applied' potential);
2. the field is turned on gradually as a linear function of time from $\tau = 0$ to τ_0 ('slow' potential).

The values of V_{max} and U will be chosen so that the system during the time evolution is numerically as stable as possible; we will return on this later. We consider chains whose number of sites N ranges from 2 to 8, in the half-filling configuration (i.e. with N electrons) and also other configurations.

We compute the exact time propagation of the many-body (MB) wave function from the time dependent Schrödinger equation using the Crank-Nicolson algorithm (5.18). As we showed in the previous chapter, this algorithm, given the wavefunction at time τ , returns the wavefunction at time $\tau + \Delta\tau$. Both the total time of the observation τ_{max} and the time-step $\Delta\tau$ have to be chosen wisely. In fact, we would want to propagate the wavefunction for a sufficiently long time so that it will be possible to see all the characteristic features of the TD system, using an enough small $\Delta\tau$ that will converge, keeping the computational cost feasible. In this work we will use

$$\tau_{\text{max}} = 10, \quad \Delta\tau = 10^{-3}, \quad (6.9)$$

where we used the Hubbard time unit (considering $\hbar = 1$ and $t = 1$, the unit of time is \hbar/t). The normalization of $|\Psi(\tau)\rangle$ was checked at each time-step and the numerical convergence was checked by modifying $\Delta\tau$. For what concern the total duration of the observation, $\tau_{\text{max}} = 10$ is comparable with

the characteristic time of transport within the chain, for the U and t considered [25]. The time of transport can be evaluated considering that, in 1D Hubbard chains, the dispersion relation for the excitations at $U = 0$ is

$$\varepsilon(k) = -2t \cos(k). \quad (6.10)$$

Eq. (6.10) yields the following group velocity:

$$v(k) = 2\frac{t}{\hbar} \sin(k). \quad (6.11)$$

Defining the total filling $n = N/m$, where N and m are the number of electrons and sites respectively, the group velocity at the Fermi momentum $k = k_F = n\pi/2$ takes the form

$$v_F|_{U=0} = 2\frac{t}{\hbar} \sin(n\frac{\pi}{2}). \quad (6.12)$$

It can be proved that, when $U \neq 0$, Eq. (6.12) has to be modified as follows [25],

$$v_F|_{U \neq 0} = 2\frac{t}{\hbar} \sin(n\frac{\pi}{2}) \sqrt{1 + \frac{U}{\pi\hbar v_F|_{U=0}}}. \quad (6.13)$$

In a m -site chain, the characteristic time of transport is simply

$$\tau_{\text{Tr}} = \frac{m}{v_F}, \quad (6.14)$$

where the proper v_F is considered.

From the TD wavefunction, we can now study the observables of interest for TDDFT. Obviously we need the charge density, which can be easily computed from (1.10). In the Hubbard model, using second quantization formalism, the electron density on each site is

$$\hat{n}_R = \hat{\Psi}_{R\uparrow}^\dagger \hat{\Psi}_{R\uparrow} + \hat{\Psi}_{R\downarrow}^\dagger \hat{\Psi}_{R\downarrow}. \quad (6.15)$$

In order to find the KS potential, we are going to compare not only the electron density, but also its gradient, the *charge current density*. It is easy to see that, being the spacial coordinate in the ‘‘Hubbard world’’ a discrete one, the charge current density is more naturally defined between sites (not

on-site as the charge density). Translating the standard definition of current in a discrete set of coordinates, we have the current $J_{R+1/2}(\tau)$ between each pair of neighbouring sites defined as

$$J_{R+1/2}(\tau) = J_{R-1/2}(\tau) + \frac{\partial n_R(\tau)}{\partial \tau}, \quad (6.16)$$

where the current densities beyond the end sites, $J_{-1/2}$ and, by implication, $J_{N-1/2}$, are zero.

In Figure 6.1 we show the charge $n_R(\tau)$ and the current $J_{R+1/2}(\tau)$ densities in a 4-site half-filled chain, for the two different time-dependent potentials, with $U = 2$, $t = 1$ and $V_{max} = 0.5$.

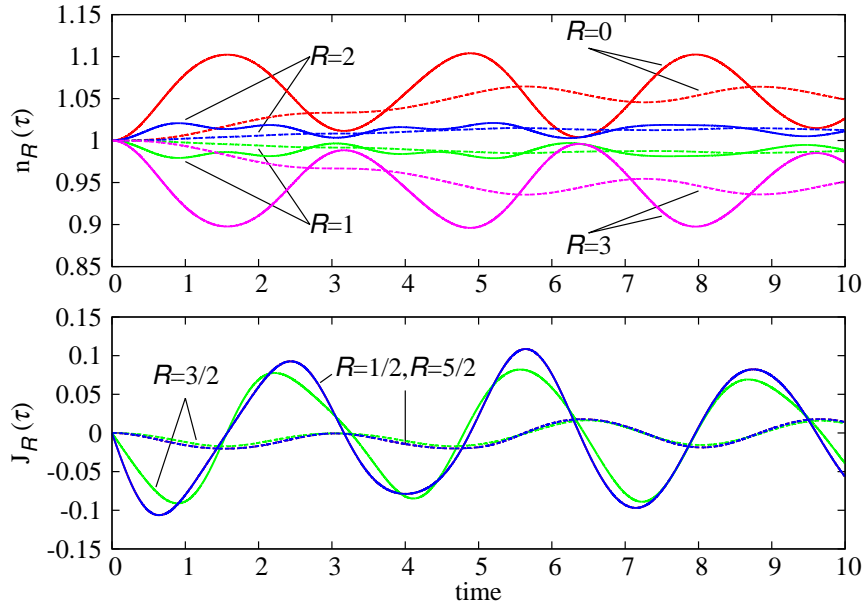


Figure 6.1: Local charge $n_R(\tau)$ and current $J_{R+1/2}(\tau)$ density for a chain with four sites and four electrons, with $U = 2$, $t = 1$ and $V_{max} = 0.5$. Full lines are for the instantaneously activated potential, dashed lines are for a slowly increasing potential where $\tau_0 = 5$. In the 4-site half-filled chain the charge density variation is symmetric and $J_{1/2} = J_{5/2}$

In the half-filling configuration, the ground-state density of the non interacting system is unity on each site. This feature is consistent with what we said in Chapter 2 about the Hubbard model: the interacting system tends to avoid configurations with doubly occupied sites. When the perturbing potential is applied, the charge density increases or decreases from one with respect to the position. Due to the symmetry of the system, the charge density variation is symmetric (i.e. $\Delta n_R(\tau) = -\Delta n_{R'}(\tau)$ where R and R' are two opposite sites with respect to the center of the chain). The inter-site current density oscillates around zero and is the same for opposite positions with respect to the center of the chain.

Away from half filling, the ground-state charge density varies from site to site while retaining its mirror symmetry; under the subsequent time-evolution the symmetry is broken, as can be seen in Fig. 6.2. Note that the currents $J_{1/2}$ and $J_{5/2}$ are no longer superimposed

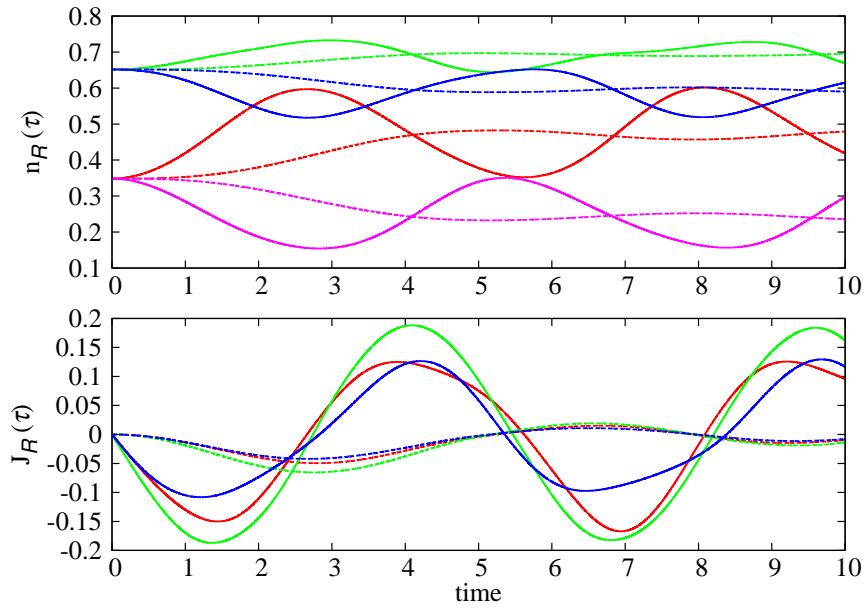


Figure 6.2: Local charge $n_R(\tau)$ and current $J_{R+1/2}(\tau)$ density for a chain with four sites and two electrons (quarter filling), with $U = 2$, $t = 1$ and $V_{max} = 0.5$. Full lines are for the instantaneously activated potential, dashed lines are for a slowly increasing potential where $\tau_0 = 5$. Unlike the half-filled chain, the charge density variation is no longer symmetric and the current densities are different. The colour scheme is the same used in Fig. 6.1

6.2 Kohn-Sham system

Let us now consider the non-interacting system that, within TDDFT, is usually called Kohn-Sham system. As we showed in Chapter 3, the philosophy of TDDFT is to define an auxiliary non-interacting system which reproduces the electron density of the interacting one, under the effect of the so-called Kohn-Sham potential (1.43). Considering that the electrons in this system are independent of each other, we can work with the wavefunction that describes just one electron in the chain. The total charge density on each site will simply be N times the charge density of one electron on that site, where N is still the number of electrons. Note that the Hubbard Hamiltonian (6.1), removed the interaction term, is spin-independent. Thus, the wavefunction contains information about the spatial coordinate only (the occupied site) and, thanks to the property of completeness, can be written as

$$|\Phi\rangle = \sum_{i=1}^N c_i |\phi_i\rangle, \quad (6.17)$$

where $|\phi_i\rangle$ is the orbital on the i -th site.

The non-interacting system Hamiltonian matrix is obviously much more simpler than the interacting one, being a $N \times N$ matrix, where N is the number of sites. The Hamiltonian ($\tau = 0$) is represented by

$$\begin{pmatrix} V_0^{\text{KS}}(\tau) & -t & 0 & 0 \\ -t & V_1^{\text{KS}}(\tau) & \ddots & 0 \\ 0 & \ddots & \ddots & -t \\ 0 & 0 & -t & V_N^{\text{KS}}(\tau) \end{pmatrix} \quad (6.18)$$

where $V_i^{\text{KS}}(\tau)$ is the Kohn-Sham potential on the i -th site at time τ . As for the interacting case, the energy of the single electron has been set to zero. Thus, the only non-zero terms are the ones on the main diagonal (potential terms) and on the first diagonal below and above it (hopping terms). The charge density on the i -th site follows directly from (6.17):

$$n_i = |c_i|^2. \quad (6.19)$$

The ground-state KS potential V_R^{KS} , which causes the non-interacting KS system to reproduce the exact ground-state density, is found via Powell's conjugate direction method [26]. As we saw previously, V_R^{KS} is the sum of the external potential V_R^{ext} and the Hartree-exchange-correlation potential V_R^{Hxc} . In the subsequent time-evolution, the KS potential is determined at each time-step so that the interacting charge and current densities are reproduced. The potential V_R^{Hxc} is defined up to an additive overall constant, so we choose its value to be zero on the left-most site in all systems studied. The optimizer computes, for each time-step, $N - 1$ (where N is the number of sites) scalar values, from the minimization of the quantity (the *cost function*)

$$\sum_{R\sigma} [(n_{R\sigma}^{\text{KS}}(\tau) - n_{R\sigma}(\tau))^2 + (\dot{n}_{R\sigma}^{\text{KS}} - \dot{n}_{R\sigma})^2]. \quad (6.20)$$

Note that we choose equal weighting for the charge and current density terms. Actually, this is not the only possible choice; the weighting of the two terms would have to be chosen in such a way that their magnitudes are comparable, and so that the minimization algorithm does not give too much importance to one of the two, neglecting the other. We choose equal weighting because this choice has proven to ensure a good numerical stability. Also the choice of using an algorithm based on Powell's method is not automatic. We stated in Chapter 5 that, if one knows approximately in which range the searched minima would have to be, is always better to use a local minimization algorithm. In this case we expect that the order of magnitude of the KS potential will be comparable with the one of the perturbing potential. Moreover, from Eq. (6.20), it is easy to see that we do not have information about the gradients of the function. Thus, Powell's conjugate direction method is the most suitable algorithm. Using the previously mentioned method, the resulting KS electron densities are always within 10^{-6} of the exact values.

The exchange-correlation potential V_R^{xc} can be obtained from the Kohn-Sham potential considering the expression

$$V_R^{\text{KS}}(\tau) = V_R^{\text{ext}}(\tau) + V_R^{\text{Hxc}}(\tau) \quad (6.21)$$

and the fact that V_R^{Hxc} consist in turn on the sum of two terms: the Hartree potential

$$V^{\text{H}}(x') = \int dx n(x) U(x - x') \quad (6.22)$$

and the exchange-correlation itself. In Hubbard systems we can rewrite the Hartree potential as

$$V^{\text{H}}(x', \tau) \rightarrow V_R^{\text{H}}(\tau) = \sum_{\sigma} n_{R\sigma}(\tau) U. \quad (6.23)$$

Subtracting the latter from $V_R^{\text{KS}}(\tau)$, V_R^{xc} is easily obtained. We are able to obtain satisfactory values of V^{xc} for moderate external fields: the KS system reproduces well the interacting system density and, for $U = 0$, V_R^{Hxc} differs from the correct value of zero by less than 10^{-6} (the latter value of U has been considered for testing the correctness of the code).

Before going on, let us discuss further the optimization process. We found out that for high values of V_R^{ext} non-physical solutions are obtained (e.g. $V_R^{\text{Hxc}} \neq 0$ also for $U = 0$) and the system is numerically unstable. This is due to the fact that at some time τ , the landscape seen by the optimizer is extremely “flat”: big variations in the KS potential cause a negligible variation of the cost function. Around these values of τ the optimizer can “jump” to solutions which are really far from the ones for the previous time steps, and for which the cost function is closer to zero for a factor of the order of numerical precision. For solving the problem we tried to add a term in the cost function which takes into account the differences between the KS potential found on each site at the current time step and the values found in the previous ones (with the aim to force the algorithm to avoid big jumps between subsequent time steps). Unfortunately, these method has proven to be ineffective, increasing numerical instability. On the contrary, using moderate values of the perturbing potential and of the interaction energy U seems to guarantee the effectiveness of the optimization process. In fact, the algorithm is stable throughout the whole time evolution considered and no sudden (and non-physical) variations in the potential are seen. For different moderate values of U , we obtain qualitatively similar results. Thus, from

now on, unless otherwise specified, we will show results only for $U = 2$, $t = 1$ and $V_R^{\text{ext}} \leq 0.5$.

In the strongly localized half-filled chains, the ground-state density of both the interacting and noninteracting systems is unity on each site, so that the ground-state V_R^{Hxc} and V_R^{xc} are both independent of R . While in the interacting system double occupations are avoided due to the interaction, in the KS system there are not energetically based arguments of this kind supporting the fact that the charge density is exactly unity on each site. In the latter case probably this feature is caused by the symmetries of the system. In these systems, for the whole range of time observed, we can see a potential V_R^{xc} that tends to screen the external perturbing field (Fig. 6.3), having a gradient with the same sign and order of magnitude as that of the Hartree potential. This behavior is in strong contrast with the LDA for which the following proportionality relations hold

$$\varepsilon_{xc} \propto -n^{\frac{1}{3}} \quad (6.24)$$

$$V_{xc} \propto -n^{\frac{1}{3}}, \quad (6.25)$$

and thus which would predict an opposite field. The slope of V_R^{xc} , after an initial increase (sites on the left) or decrease (sites on the right) from zero, varies slightly in time and space around the value of the ground-state exchange-correlation potential for the perturbed Hamiltonian $V_R^{\text{pgs-}xc}$ (where the perturbing potential is V_R^{ext}), giving rise to a ladder-like form.

Chains in the quarter-filling configuration, or similar configurations for an odd number of sites, show a quite different behaviour: the KS system ground state n_R is different from the one of the interacting system. Thus, the ground state V_R^{xc} is already non-zero. V^{xc} no longer adopts the form of a screening electric field, and its spatial variation is concentrated towards the ends of the chain; its relationship to the local density reflects a more LDA-like behaviour (Fig. 6.4). (The ‘slow’ external potential gives qualitatively similar results.)

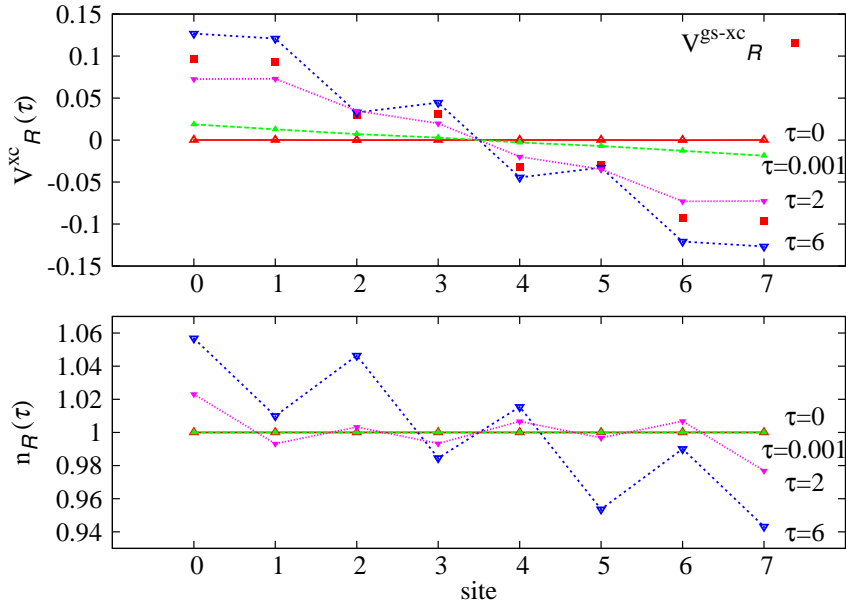


Figure 6.3: Exchange-correlation potential and charge density, in function of the position for different times τ , for a half-filled 8-site chain subjected to an instantaneously applied $V_R^{\text{ext}}(\tau)$. When V_R^{ext} is applied, V_R^{xc} acquires a non-zero slope in the first time-step, even though the charge density is essentially indistinguishable from that of the ground state $n_R(0)$. At later times, V_R^{xc} slightly varies around the ground-state exchange-correlation potential of the perturbed Hamiltonian V_R^{pgs-xc} .

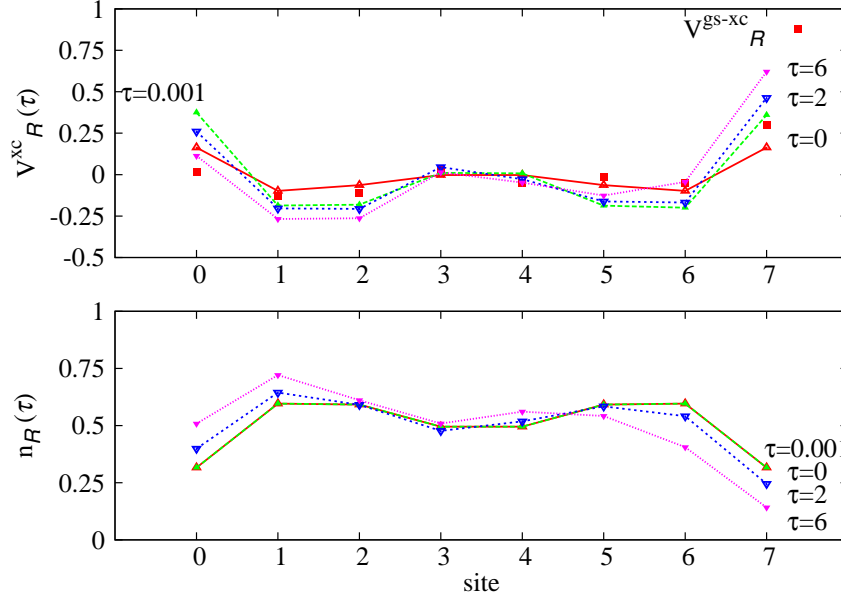


Figure 6.4: Exchange-correlation potential and charge density, in function of the position for different times τ , for a quarter-filled 8-site chain subjected to an instantaneously applied $V_R^{\text{ext}}(\tau)$. V_R^{xc} shows a different behaviour with respect to the half-filled case: there is no screening electric field and the spatial variation is concentrated towards the ends of the chain (more LDA-like behaviour). The features concerning the first time-step and the relation between the potential and $V_R^{\text{pgs-xc}}$ seen in the half-filled chains still hold.

6.3 Adiabatic and instantaneous ground state

$$V^{\text{xc}}$$

We compare the exact $V_R^{\text{xc}}(\tau)$ with two approximate potentials based on the notion of adiabatic correctness of ground-state DFT for sufficiently slowly varying external potentials: (a) the ‘adiabatically exact’ exchange-correlation

potential $V_R^{\text{Ad-xc}}(\tau)$ for which the ground-state charge density of the non-interacting system at each τ is equal to the actual instantaneous many-body charge density, and (b) the ‘instantaneous ground-state’ exchange-correlation potential $V_R^{\text{igs-xc}}$ for which the ground-state charge density is equal to that of an interacting system subjected to the actual instantaneous *external potential*. (For the instantaneously applied external potential, $V_R^{\text{igs-xc}}$ therefore corresponds to the time-independent $V_R^{\text{pgs-xc}}$, which was shown in Figs. 6.3 and 6.4 by red dots.) In the limit of a truly slowly-varying perturbing potential, both approximations should be identical, because the instantaneous charge density will be the ground-state charge density of the instantaneous external potential. Comparing the two different types of potential, we are going to investigate whether, in the case of a not so slowly-varying perturbing potential (in our case, abruptly switched on at full strength at $\tau = 0$), the density or the external potential is the more secure quantity on which to base an adiabatic approximation. We will show briefly that the answer is the external potential. In fact, the instantaneous density, because it is in reality not the ground state of the instantaneous potential, corresponds to the ground state of a rather peculiar Kohn-Sham potential which is rather different from the exact instantaneous Kohn-Sham potential. This is an example of the well-known general sensitivity of V_{KS} (V_{xc} in particular) to changes in the charge density. Whereas in the $V_R^{\text{igs-xc}}$ approximation one is simply assuming that the exchange-correlation part of the Kohn-Sham potential is described reasonably well by the form that it takes in the ground state of the instantaneous external potential, which, although an approximation, does not suffer from the above-mentioned sensitivity.

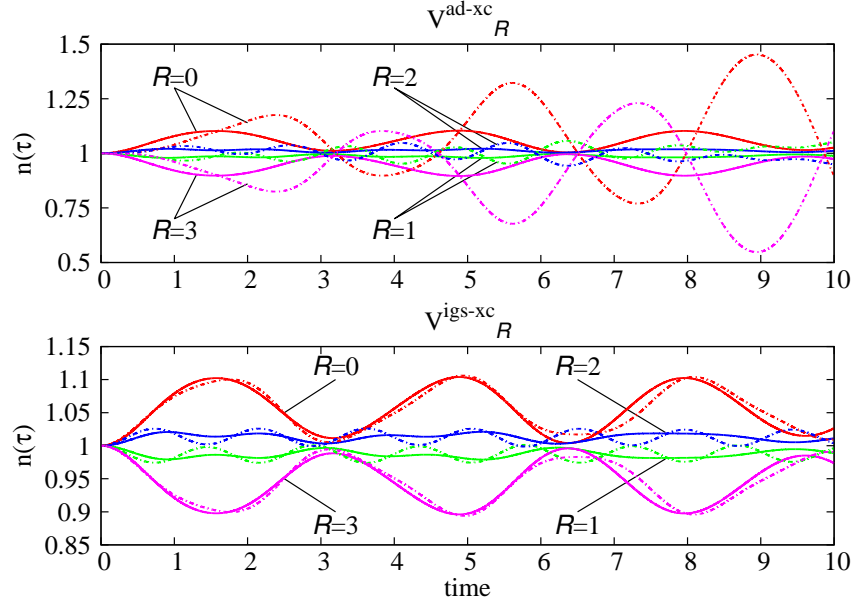


Figure 6.5: Exact many body charge density (full lines) and approximated charge density (dashed lines) for a 4-sites half-filled chain subjected to the ‘instantaneously applied’ $V_R^{\text{ext}}(\tau)$. obtained using the two approximated potentials $V_R^{\text{Ad-xc}}(\tau)$ and $V_R^{\text{igs-xc}}$. The latter is a surprisingly good approximation even for a fast applied field, while the former is not able to reproduce the exact density (consistently with the adiabatic theorem).

We apply these two approximations to half- and quarter-filled chains, considering both ‘instantaneously applied’ and ‘slow’ external potentials. In half-filled chains, for the ‘instantaneously applied’ potential, $V_R^{\text{igs-xc}}(\tau)$ works extremely well in reproducing the exact density, while the adiabatically exact approximation results are strikingly poor (Fig. 6.5). The fact that the latter does not work properly is not an unexpected outcome: as we saw in Chapter 3 an adiabatic approximation is expected to be good only for slowly varying systems, owing to the adiabatic theorem. For the slower perturbing

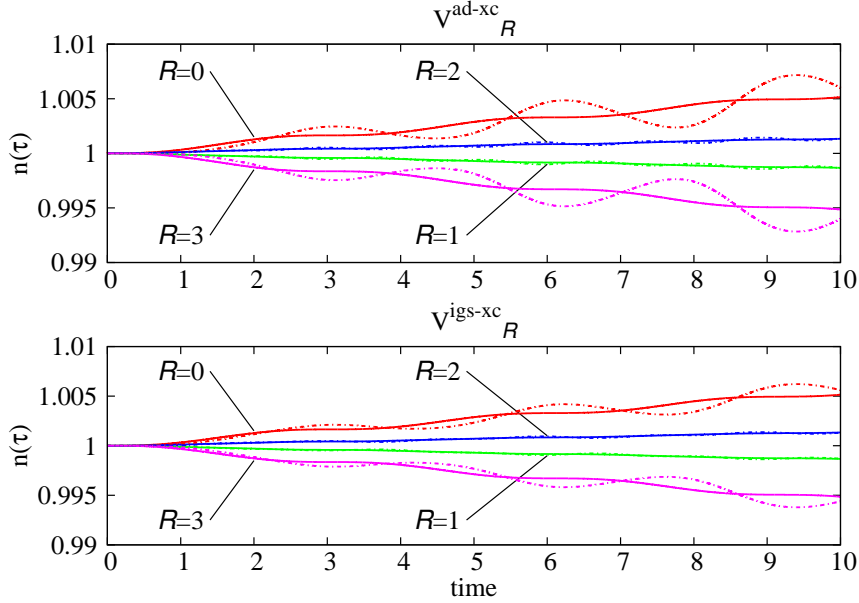


Figure 6.6: Exact many body charge density (full lines) and approximated charge density (dashed lines) for a 4-sites half-filled chain subjected to a ‘slow’ $V_R^{\text{ext}}(\tau)$. obtained using the two approximated potentials $V_R^{\text{Ad-xc}}(\tau)$ and $V_R^{\text{igs-xc}}$. The density reproduced by $V_R^{\text{igs-xc}}$ is closer to the real one than the density reproduced by $V_R^{\text{Ad-xc}}(\tau)$.

potentials, both $V_R^{\text{Ad-xc}}(\tau)$ and $V_R^{\text{igs-xc}}(\tau)$ perform exceptionally well, once the potential changes sufficiently slowly, with $V_R^{\text{igs-xc}}(\tau)$, once again, giving a better approximation than $V_R^{\text{Ad-xc}}(\tau)$ (Fig. 6.6). (For studying the range of applicability of the adiabatic approximation, different velocities of variation have been considered: if the potential is applied slowly enough, the relative difference between the exact and the approximate density is independent of the speed of variation.) It appears that the character of the strong correlation present in the half-filled Mott-Hubbard-insulating chains is relatively resistant to time-dependent excitation, and remains well described by the *ground* state of the instantaneous external potential. In contrast, in the less

strongly-correlated quarter-filled chains, neither adiabatic approximation is good, even for extremely slowly-varying potentials.

6.4 Failure of the local approximations

In order to study the feasibility of an approximation for the exchange-correlation potential based on the local electron charge density (in the philosophy of the LDA) and the local current density, we examine the relation between $V_R^{\text{xc}}(\tau)$, $n_R(\tau)$ and $J_R(\tau)$. For this purpose, the on-site current density $J_R(\tau)$ is defined as the average value of the two inter-site current densities $J_{R+1/2}(\tau)$ surrounding the site (using zero beyond the chain ends). We are also interested in the dependence of the non-equilibrium part of the KS electric field on the local current density, as suggested by Ref. [27] on the basis of calculations for a model semiconductor. We first consider the dependence of V^{xc} on the local n and J . In Fig. 6.7 we show the relation between $V^{\text{xc}}(\tau)$, $n_R(\tau)$ and $J_R(\tau)$ for the four-site half-filled chain subjected to the fast $V^{\text{ext}}(\tau)$. In this configuration the ground-state V^{xc} is zero, so that the plotted quantity coincides with the dynamical part of the potential. If a dependence of V^{xc} on the local densities exist, it would have to be possible to plot the potentials parametrized on τ for the different sites on an universal surface with respect to n_R and J_R . In analysing the results of Fig. 6.7, we have to remember that the exchange-correlation potential is defined up to an additive TD constant. Thus, for the argument previously mentioned to hold, we would have to be sure that the universal surface does not exist even considering the possibility of adding at each τ a different constant to the potential. Helping ourselves with the projections shown in the figure, we can easily see that there are no ways for plotting the potentials for each site on the same surface due to their specular symmetry.

Looking at V^{xc} in the early time-steps, we can find another argument against the feasibility of a local approximation. We have shown that in half-filled chains the ground-state charge density of the KS system is unity on each

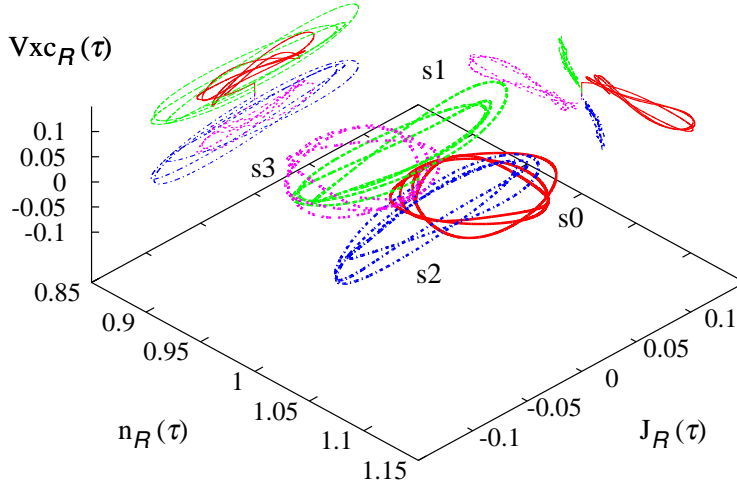


Figure 6.7: Exchange-correlation potential $V_R^{xc}(\tau)$ for a 4-sites half-filled chain subjected to an instantaneously applied perturbing potential, with $U = 2$, $t = 1$ and $V_{\max}^{\text{ext}} = 0.5$, plotted over the local density $n_R(\tau)$ and the on-site density current $J_R(\tau)$. For an approximation of V^{xc} based on the local values of n_R and J_R to hold, it would have to be possible to plot the potential on an universal surface (the same for all the sites) with respect to one of the two quantities. The projections onto the V^{xc} - J and V^{xc} - n planes are also shown; these serve to clarify the spatial form of the trajectories, and also directly illustrate the limitations of local approximations based on n and J only, respectively.

site, as it is for the interacting system. Thus, the KS potential is the same on each site. After the first time-step, it is possible to see a sudden change in V^{xc} , which is not simply due to the discretization of $\Delta\tau$ and that is not reflected in charge and current densities. This implies that an approximation based on the local values of the densities would not be able to reproduce this feature of V^{xc} . Even if in quarter-filled chains the exchange-correlation potential shows a more LDA-like behaviour, it is still not possible to find an universal surface.

In Fig. 6.8 we show, similarly as the previous case, the dependence of the dynamical part of $V^{xc}(\tau)$ on $n_R(\tau)$ and $J_R(\tau)$ for the four-site quarter-filled

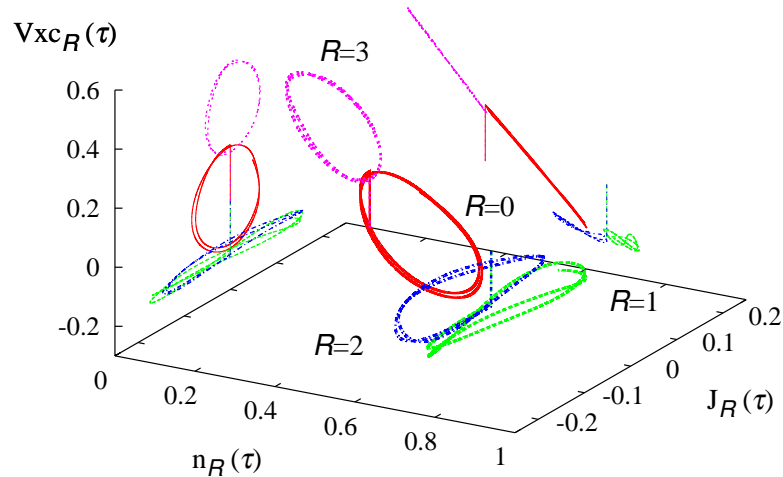


Figure 6.8: Dynamical part of the exchange-correlation potential $V_R^{xc}(\tau)$ for a 4-sites quarter-filled chain subjected to an instantaneously applied perturbing potential, with $U = 2$, $t = 1$ and $V_{\max}^{\text{ext}} = 0.5$, plotted over the local density $n_R(\tau)$ and the on-site density current $J_R(\tau)$. In contrast with the half-filled case, the potential shows an almost LDA like behavior.

chain subjected to the fast $V^{\text{ext}}(\tau)$. In this case the ground-state potential is different from zero. Thus, the dynamical part of the latter is obtained subtracting $V^{xc}(\tau = 0, R)$ from the respective on-site potentials. From the graph it is possible to see that, apart from a sudden jump corresponding to the application of the external field, the curves tend to show a local dependence on $n_R(\tau)$, consistently with what shown in Fig. 6.4

Let us now consider the alternative local strategy of approximating V_R^{xc} as the sum of two parts: one based on the local density and the other whose *gradient* is based on the local current. We write

$$V_R^{xc} = V_R^{xc-n} + V_R^{xc-J}, \quad (6.26)$$

where

$$V_R^{\text{xc}-n} = a_0 + a_1 n_R \quad (6.27)$$

$$\nabla V_R^{\text{xc}-J} = b_0 + b_1 J_R. \quad (6.28)$$

Note that we consider only terms of the first order in the expansion. When we introduce additional degrees of freedom into our fit, we would expect to get a "better" fit (i.e. a closer fit), but actually we may be "overfitting" in the sense that the fit is not meaningful when used to predict values outside the "training set" of data. Moreover, it is more convenient to consider

$$\nabla V_R^{\text{xc}} = \nabla V_R^{\text{xc}-n} + \nabla V_R^{\text{xc}-J}, \quad (6.29)$$

so that all the quantities are naturally defined between sites (so that R is a half-integer), and write

$$\nabla V_R^{\text{xc}-n} = a_1 \nabla n, \quad (6.30)$$

where

$$\nabla n = n_{R+1/2} - n_{R-1/2}. \quad (6.31)$$

By symmetry (for an universal approximation) b_0 must be zero, because $\nabla V_R^{\text{xc}-n}$ and $\nabla V_R^{\text{xc}-J}$ must both be odd functions of Δn and of J : if system **A** has densities $n(x)$, $j(x)$ and potential $V^{\text{xc}}(x)$, and system **B** has densities $n(-x)$, $j(-x)$, then obviously **B** has $V^{\text{xc}}(-x)$.

We use an algorithm based on Powell's method for finding the best universal coefficients a_1 and b_1 for fitting with this approximate ∇V^{xc} the exact one, considering several different systems in half-filling and quarter-filling configuration. The optimization process is unable to find a pair of coefficients that represents our potentials with any degree of accuracy even for one system, let alone a universal pair of coefficients that applies to all the systems studied.

6.5 Correlation

we stated in Chapter 4 that the pair correlation function provides direct insight into the nature of the electronic correlation. The PCF can be written

$$\Gamma_{\sigma,\sigma'}(R, R') = \langle \psi | n_{R,\sigma} n_{R',\sigma'} | \psi \rangle / (n_{R,\sigma} n_{R',\sigma'}). \quad (6.32)$$

(if $R = R'$ and $\sigma = \sigma'$, $\Gamma = 0$). We consider the on-site PCF ($\uparrow\downarrow$). In this case, if $U = 0$, the PCF is equal to one for each R . Increasing the interaction, its ground-state value decreases towards zero. This is clearly consistent with the interpretation of the PCF as the probability of finding an electron in R' if there is one electron in R . In general, if one considers half-filled chains, the most striking features of $\Gamma_{\sigma,\sigma'}(R, R)$ is that its value varies only slightly during the time evolution with respect to the ground-state value for higher magnitudes of U : the nature of the electronic correlation is, to a good approximation, frozen in its ground-state form (Fig. 6.9). On the other hand, quarter-filled chains shows quite a different behaviour: in this case, as can be seen in Fig. 6.10 the nature of the correlation shows a stronger time dependence, which also characterizes the electron density n . This feature seems to be consistent with the good results obtained using the instantaneous-ground-state exchange-correlation potential $V_R^{\text{igs-xc}}(\tau)$ as an approximate KS functional.

6.6 Half-filled chains with negative interaction

We have stated in the previous chapters that one of the most important characteristics of the Hubbard model is that in the half filling configuration the system behaves as a Mott insulator. The insulating properties of the latter, instead of being due to the presence of a completely filled band, are an effect of the lattice and of the charge density properly tuned (unity on each site) for opening the charge gap [25]. We are interested in seeing if

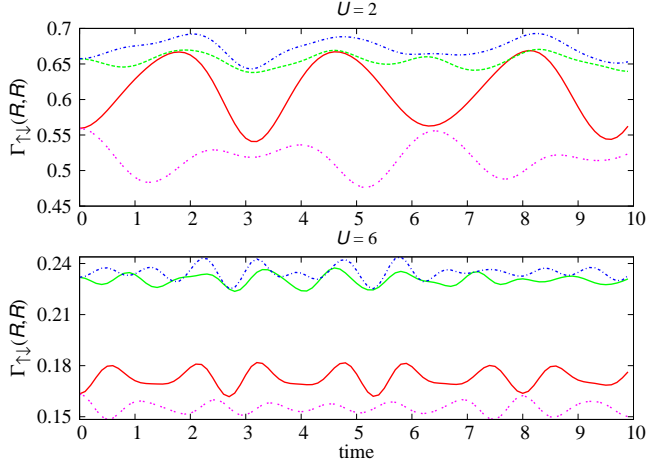


Figure 6.9: On-site pair correlation function in function of time for a four sites chain in HFC. Passing from $U = 2$ to $U = 6$, the ground state $\Gamma_{\uparrow,\downarrow}(R, R)$ decreases and the variations of the PCF during the time evolution with respect to the ground state value are smaller.

it is possible to leave the insulating regime in the lattice. In the standard Hubbard model there are few ways for achieving this result: one can act on the filling conditions (as we have already done in studying for example quarter-filled chains), or can change the value of the interaction U . Until now, we have been using positive value of U . This is the most logical choice if the Hubbard chains are used for modeling real electronic systems (in this case U is the Coulomb interaction). However, we have seen in Chapter 2 that in optical lattices it is possible to fix negative values of the effective interaction U through Feshbach resonances. A negative value of the interaction allows to obtain the so-called *Luther-Emery phases*, or phases which are characterized by a spin gap, but that do not show a charge gap [28].

In Figure 6.11 we show the computed exchange-correlation potential and density for a four-sites half-filled chain, where a negative value of the interaction ($U = -2$) has been used. The potential is clearly similar to

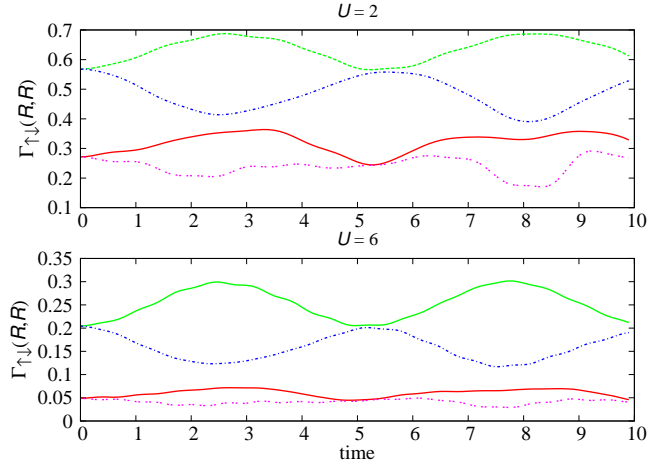


Figure 6.10: On-site pair correlation function in function of time for a four sites chain in QFC. Passing from $U = 2$ to $U = 6$, the ground state $\Gamma_{\uparrow,\downarrow}(R, R)$ decreases going towards higher values of U , but the variations of the PCF during the time evolution with respect to the ground state value are not smaller as in half-filled chains.

the one observed previously for half-filled chains with positive U . In fact, it is still possible to see the screening electric field in contrast with LDA, but the main difference is in the shape of the potential: there is no longer the ladder-like structure and the on site potential seems to be more strictly proportional to the density. The latter feature can be more easily seen in Fig. 6.12. The plots are almost on a same surface with respect to n , but its gradient is positive, in contrast with common LDA, for which it would have to be negative (as seen in Fig. 6.8). Finally, we compute the PCF for the case of half-filled chain with negative value of U . In Figure 6.13 is plotted the on-site pair correlation function for $U = -2$ and $U = -6$. From this graph we can see that the correlation Γ is spread over a range of values quite different with respect to the case $U > 0$. In particular, a great increase can be seen for $U = -6$, which cannot be easily interpreted. Probably is due to the term at the denominator of (6.32), and the fact that for a negative U , even if in half filling configuration, pairs of electrons tend to move together,

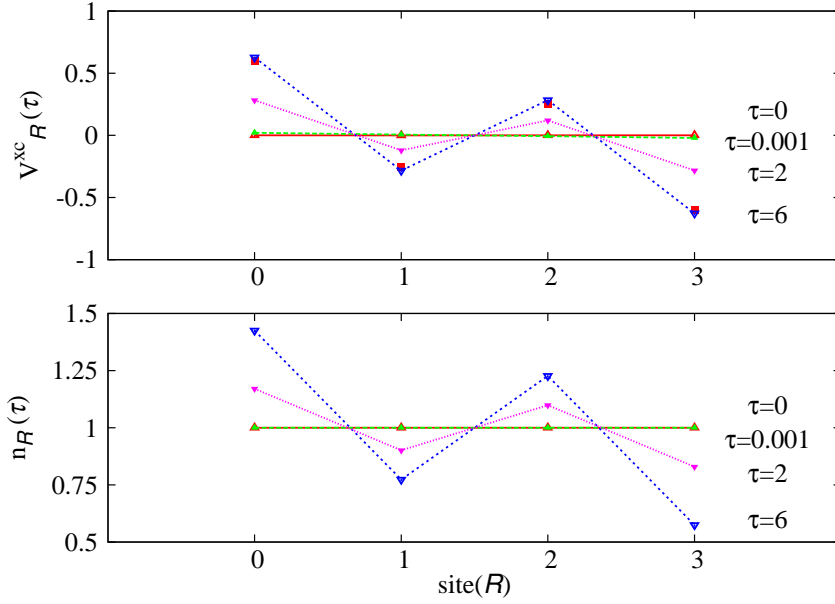


Figure 6.11: Exchange-correlation potential and charge density, in function of the position for different times τ , for a half-filled 4-site chain subjected to an instantaneously applied $V_R^{\text{ext}}(\tau)$ and for $U = -2$. V_R^{xc} shows a similar behavior with respect to the previously seen eight-sites half-filled case: there is still the screening electric field, but the potential does not show the ladder-like shape and seems to be strictly proportional to the density (note however that the sign of the proportionality relation is opposite to the one predicted by common LDA).

leaving empty sites during the evolution.

From the data we obtain, it seems that a local approximation for V_R^{xc} , dependent on the values of n and J , would be more effective for $U < 0$, where the charge gap is null and some (superconductive) density correlations would have to be amplified with respect to the repulsive case. For this reason, we are not able to draw a robust interpretation of these phenomena. We hope that further studies on the topic will be able to get more insight on these aspects of the Hubbard model.

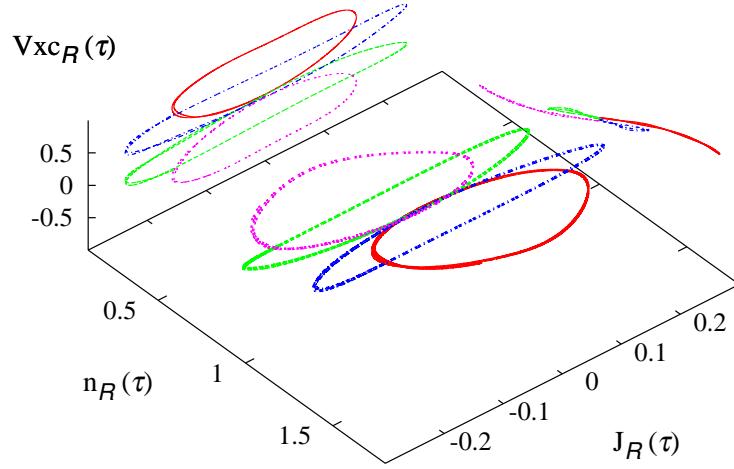


Figure 6.12: Dynamical part of the exchange-correlation potential $V_R^{xc}(\tau)$ for a 4-sites half-filled chain subjected to an instantaneously applied perturbing potential, with $U = -2$, $t = 1$ and $V_{\max}^{\text{ext}} = 0.5$, plotted over the local density $n_R(\tau)$ and the on-site density current $J_R(\tau)$. The potential shows an almost local dependence on n , but the sign of this dependency is positive, in contrast with what we have seen previously in quarter-filled chains.

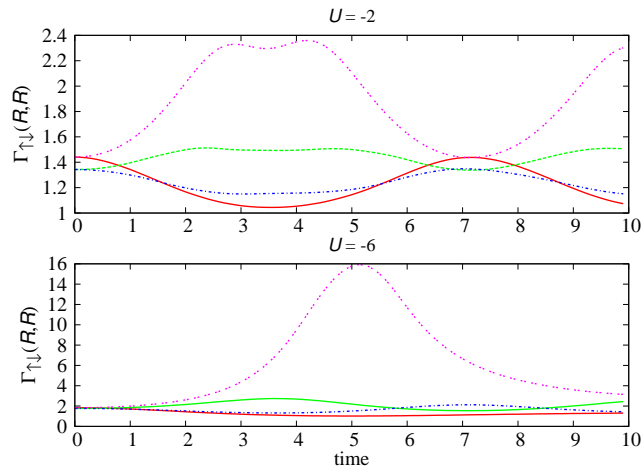


Figure 6.13: On-site pair correlation function in function of time for a four sites chain in HFC. Passing from $U = -2$ to $U = -6$

Conclusions

In conclusion, we have shown that in half-filled Hubbard chains the correlation of the system is dominated (especially for larger U) by the strongly localized ground-state. Direct consequence of this feature are that approximate exchange-correlation potentials based on the instantaneous values of the external potential are generally better than the ones based on the instantaneous charge density, particularly in the sudden approximation, and that these approximations perform remarkably well even when exact adiabatic approximations fail. The former result, albeit it holds in absolute terms only for certain filling schemes, can be of help in defining suitable approximate functional for systems in which the correlation of the ground-state plays a particularly important role for the subsequent time evolution.

The effectiveness of the former approximate functional, and its interpretation as an effect of the leading role of the ground-state correlation, are consistent with the computed form of the pair correlation function. This consistency shows that the pair correlation function is an extremely useful tool for getting some insight into the system correlation, and consequently for obtaining supplementary information that can be of great aid in defining feasible approximate functionals.

On the other hand, for quarter-filled chains, both types of adiabatic functional are unable to reproduce the exact density due to stronger time dependence of both the density itself, and the nature of the correlation. The differences between the performances of adiabatic approximate functionals in half-filled systems and other filling schemes reflect the well known electron

localization which characterize Hubbard systems in the former filling scheme. Unfortunately, this particular feature of the “Hubbard world” makes uneasy to understand if phenomena observed in these model systems can be generalized to more realistic models and real systems.

Finally, we have shown that approximate functionals based on the local value of the electron charge and current density perform poorly in both half and quarter-filled systems. The nonlocality of these functional was somehow expected. In fact, even in the ground state, the existing DFT functionals are nonlocal in n and J . The strongly localized nature of the model does not seem to be sufficient to introduce local dependencies in the exchange-correlation potential.

Future research activity may be envisaged in various directions. A possible line of studying would be to investigate more deeply the functional dependence of V_{xc} on n and J . Investigations on this type of dependence are currently under study for more realistic model systems, and it would be interesting to see if features seen in the latter systems hold also for Hubbard chains. As a second direction, it would be of great interest to further study the correlation of the system and its relation with approximate adiabatic, and non adiabatic functionals. Finally, more information about TDDFT functionals might be obtained extending the methodology used in this thesis work to 2D Hubbard lattices and 3D Hubbard systems.

We hope that this study will encourage further investigations of TDDFT for Hubbard systems, and that it can help in establishing the role of the Hubbard model as an interesting tool for developing new strategies for defining approximate DFT functionals.

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