Ensemble Density Functional Theory on a Lattice.

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Declaration

I, the undersigned, hereby declare that the work contained in this PhD thesis is my original work, and that any work done by others or by myself previously has been acknowledged and referenced accordingly. This thesis has not been submitted before for any degree or examination in any other university.

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Abstract

Density Functional Theory (DFT) is an elegant reformulation of quantum mechanics in which the density distribution is the variable that formally contains all the information about a system. It was placed on a formally sound theoretical footing by Hohenberg and Kohn [1] in 1964 and an implementation for determining the ground state density and energy was proposed by Kohn and Sham the following year [2]. Despite more than fifty years since Hohenberg and Kohn showed that the density can be used as the controlling variable, there is no known exact way to implement DFT. Nevertheless, DFT has been successfully applied using approximations and has become the standard approach for investigating structural properties of solids and molecules. In this project we examine properties of DFT functionals for a finite single band Hubbard chain. The advantage of using a Hubbard model is that for short chains exact solutions can be found numerically and for a uniform infinite chain an analytic solution is available. The exact solutions can be used as a reference for approximate implementations of DFT. We explore DFT on a lattice in an ensemble formulation which allows a formal implementation of DFT for fractional particle numbers. We show that even for a simple uniform density approximation the resulting functional derivatives have a spatially independent discontinuity as a function of particle numbers at integer particle number, as the required by the exact formalism. An approximate exact implementation of Kohn-Sham DFT with the neglect of the DFT correlation energy can be implemented exactly and results show that it can compare very well with the exact solution, but that the success of the approximation is not consistent under all circumstances. Finally we show that it is possible to achieve the original goal of Kohn-Sham Density Functional Theory which was to find the ground state density and energy of an interacting system while all calculations are performed for a fictitious independent particle model. We introduce a mapping of the ground state wavefunction basis function expansion coefficients of a single band Kohn-Sham Hubbard model onto the coefficients of the interacting Hubbard model and derive a set of exact self-consistent equations that can be solved within an fictitious Kohn-Sham framework to find the interacting ground state density and energy.

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Chapter 1

Introduction

In physics, many body problems emerge frequently from the attempt to understand solid and molecular structures and properties. The elementary particles involved in these studies are the nuclei and electrons of atoms. The complexity of many-particles systems increases exponentially with the size of the system under consideration.

The first significant insight into breaking down this complexity arises from the work of Born and Oppenheimer [3, 4] called the Born-Oppenheimer (BO) approximation. However, instead of addressing the real system, they deduced from the experimental observations that energy levels of molecules mimic an electronic system with electrons rotating around a semi-rigid nucleus and that the nuclear kinetic energy is negligible compare to the electronic kinetic energy. Therewith the presence of nuclei in the system resembles an external potential in which the electrons move. On the other hand, the potential generated by nucleus-nucleus interactions is mapped to a parameter that contributes to the total energy of the system. This type of approximation at its beginning had been criticized [4, 5] for being introduced without a solid analytical demonstration and for its probable inaccuracy to highly predict molecular systems. However, it underlies various reliable modern approximations. For instance, the Hartree method [6, 7] aims to obtain the ground state wave function by solving the electronic Hamiltonian resulting from the BO approximation.

In 1923, Douglas Hartree got the genius idea to express the wave function of a many-electron system as a product of single-electron wave functions solution of the Schrödinger equation wherein the operator that couples electron-electron interactions is removed. Doing so, he unveiled the existence of a self consistent field, called the Hartree potential. Like the wave function, Hartree potential becomes the primary target when implementing this method. Nevertheless, this new method quickly reached its limitation since its ground state violates the Pauli's exclusive principle whenever the system under consideration contains more than one electron. Fock [8, 9] used the same approach as Hartree, but instead of a single product he opted for the determinant method of Wigner [10, 11, 12, 13] that inherits the antisymmetry property of the determinant operator. It is worthy to mention that, because Fock's approach involves electron spins, the method turns out to yield the so called exchange potential. At that stage, the form of the wave function included all the basic properties necessary to satisfy the endeavour of scientists in related fields. However, slight variation of the self consistent potential field regarding the electron as a subject failed to come up with fully expectations till 1950 when Slater [14, 15, 16] finally made the field unique regardless of the electrons by weighing and averaging the

exchange potential on one hand, and on the other hand making use of the slater determinant and a fictitious non-interacting system. (The use of Slater determinant has the merit to simplify the understanding of the mathematics used by Fock when he was trying to redress Hartree's method.) These final refinements have sharpened enough the Hartree-Fock method which became a sustainable tool to probe many-electron systems for physicists and chemists. It succeeds in reducing considerably the effort needed with respect to the number of particles involved in the problem. Indeed, for each electron there is a four dimensional ($\mathbb{R}^3 \times \{\uparrow, \downarrow\}$) variable so that for a n_e particle system the dimension of the wave function is 4^{n_e}. Consequently, a small increase in the particle number will exponentially toughen the computational efforts. This is what Kohn [17] has called the exponential wall.

Another breakthrough comes with the emergence of DFT (Density Functional Theory), an ab initio approach, that instead of seeking for wave functions looks for the electronic density distribution over the configuration space. DFT was primitively used at the same time by Thomas and Fermi (TF) in 1927 [18]. Thomas, conscious of the difficulty that researchers have to figure out the effective potential which fits with the experimental data of particular systems, introduced the notion of uniform distribution of electrons. Thus, he was able to recover the effective field that ought to be considered. However, this was not accurate enough since from the beginning it failed to be realistic. Indeed, it is clear that electron repartition will not be easily fitted by a uniform distribution. Fortunately, TF (Thomas and Fermi) method has been improved to the venerable approximation called Local Density Approximation (LDA) and its hybrids [19, 20]. DFT really started with the works of Kohn, Hohenberg and Sham in 1960. Kohn and Hohenberg [1], formally set the total energy as a functional of the electronic density of the system. From this formalism, they proved that the energy can only reach its minimum at the ground state density. Nonetheless, their work does not help in practice. Not long afterwards, Kohn with Sham (KS) [2] found that it is necessary to define a new type of correlation that they simply called correlation energy while considering a fictitious noninteracting system which ground state density is equal to the interacting density. (The common name is the exchange-correlation (XC) energy to mean the addition of the exchange and the correlation energy.) The XC energy is indeed the fraction that has to be added to the kinetic, the Hartree and the external potential energy in order to obtain the total energy of the interacting system. Alongside the ongoing discussion around DFT and even doubt about the existence of a well defined XC energy [21], the XC energy has been used to explain the problem of calculating the fundamental band gaps [22, 23] encountered in insulators and semiconductor materials. The KS formalism does not provide an exact form of the XC energy density functional. Therefore, DFT relies on approximations though there is not a systematic way to achieve this. In return, different approximations have been implemented in the literature. The standout approximations over the years include: the LDA, the Generalized Gradient Approximations (GGA) [22, 23] and the Hybrid functionals [24, 25, 26]. These approximations are elaborated to respond to specific problems. Their built-in density functionals is designed upon known properties of the target functionals and so their field of application is limited. It becomes imperative to further probe density functionals properties. Hopefully, one can assess the formalism and gain insight into the properties of DFT by investigating solvable models.

Lattice-DFT [27, 28] is probably one of the best models where DFT theories can be accurately assessed. The simplest of these is the one-dimensional Hubbard model [29, 30, 31]. Although it is not possible to find a general analytical solution, it exists for special cases. For small systems Exact

Diagonalization (ED) of the Hubbard model is feasible and that is the approach we chose. Within the KS scheme, it is instructive to work out the effective Kohn-Sham potential for the Hubbard model self-consistently, to check its dependence on the number of particles (specifically for integer particle numbers) and furthermore to investigate the exchange-correlation energy or potential as a function of fractional particle numbers in an ensemble formalism. Nevertheless, a knowledge of the total energy is necessary to fully study the exchange-correlation energy. Thus, in the attempt to address this challenge, we acted on the KS ground state wave function by a Jastrow factor that will provide it with more correlation. One can establish a self-consistent approach, that we call exact method, to get the factor for any integer number of electrons. As expected, the exact method amazingly and accurately returns the total energy and the interacting density. It also returns the interacting ground state wave function exactly. We derived an explicit expression of the correlation potential and energy with regard to the Jastrow factors.

In Chapter 2, we focus on the fundamentals that promote the rise of DFT by recapitulating some known results. From the definition of ensemble DFT, we give a brief analytical discussion on the spatially independent discontinuity of the KS potential at integer particle numbers. We study the discontinuity of the kinetic energy and its derivative as well. Analytical results that underline the different methods stated in this Chapter are detailed in Appendix *A*. Chapter 3 follows with the concept of Lattice-DFT and its backgrounds relevant for this thesis. Interested in small lattice systems, we briefly review finite dimensional Hamiltonians while focussing on the ground state properties of the one dimensional Hubbard Hamiltonian. To illustrate this, we perform an exact diagonalization based on an exact KS scheme which yield the KS potential. (More results for a two site lattice is expanded in Appendix B.) We therefore numerically study the discontinuity of the KS potential in Chapter 4. We show that the LDA used in [32] does not highlight this discontinuity. We explore in Chapters 5 and 6 two new approaches: the Hartree plus exchange and the Jastrow factor approximations respectively. The first produces excellent results for the approximate KS kinetic energy while the result is acceptable for the density. The second simply returns exact numerical results of the interacting ground state. A thorough summary and perspective are included in Chapter 7.

Chapter 2

Density Functional Theory: Underlying theory

This chapter summarizes the relevant underlying concepts that progressively lead to the birth of DFT. Starting from the Born Oppenheimer approximation, which allows us to study electrons in isolation as a first approximation, it narrates how concepts developed to improve the theory that culminated in formal DFT as proposed by Walter Kohn and co-workers in the mid 1960's.

2.1 Born Oppenheimer Approximation

If we exclude relativistic effects the Hamiltonian of a many-atom system is given by

$$\hat{H} = \hat{T}_n + \hat{v}_n + \hat{T}_e + \hat{u} + \hat{v}_{n-e}, \tag{2.1}$$

where

$$\hat{T}_n = -\frac{\hbar^2}{2m_n}\sum_{i=1}^{m}\nabla^2_{\mathbf{R}_i} \tag{2.2}$$

is the nucleon kinetic energy operator,

$$\hat{T}_e = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n_e}\nabla^2_{\mathbf{r}_i} = \sum_{i=1}^{n_e}\hat{T}_i \tag{2.3}$$

is the electron kinetic energy oprator,

$$\hat{v}_n = \frac{e^2}{4\pi\epsilon}\sum_{i=1}^{m}\sum_{i<j=1}^{m}\frac{Z_i Z_j}{\mid \mathbf{R}_j - \mathbf{R}_i \mid} \tag{2.4}$$

is the nucleon-nucleon potential operator,

$$\hat{u} = \frac{e^2}{4\pi\epsilon}\sum_{i=1}^{n_e}\sum_{i<j=1}^{n_e}\frac{1}{\mid \mathbf{r}_j - \mathbf{r}_i \mid} \tag{2.5}$$

is the electron-electron potential operator and

$$\hat{v}_{n-e} = -\frac{e^2}{4\pi\epsilon}\sum_{i=1}^{n_e}\sum_{j=1}^{m}\frac{Z_j}{\mid \mathbf{R}_j - \mathbf{r}_i \mid} \tag{2.6}$$

is the nucleon-electron potential operator. In the equations above, m stands for the number of nuclei and $\mathbf{r}_i$ and $\mathbf{R}_j$ (in $\mathbb{R}^3$) stand for the coordinates of the i^{th} electron and the j^{th} nucleon respectively. m_n is the mass of a nucleon and m_e the mass of an electron. In the following $\mathbf{x} = (\mathbf{r}, \sigma)$ and $\mathbf{X} = (\mathbf{R}, \sigma)$ will be used as compound electron position and spin coordinates and nucleon position and spin coordinates respectively. The Hamiltonian in Eq. (2.1) allows one to tackle the Schrödinger equation,

$$\hat{H}\Psi(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e}) = E\Psi(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e}) \tag{2.7}$$

which yields a set of eigenfunctions Ψ with their corresponding eigenenergies. In this thesis we are primarily interested in the minimum eigenenergy, the ground state energy, and its eigenfunction, the ground state wave function. Here Ψ is used interchangeably for all (when in equations) and the ground state wave functions. The meaning of Ψ will be evident from the context.

The basis of the BO approximation is the assumption that all eigenstates of Eq. (2.7) can be expressed as the product of two eigenstates. To highlight this, let us consider the electronic Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{u} + \hat{v}_{n-e} \tag{2.8}$$

so that

$$\hat{H} = \hat{T}_n + \hat{v}_n + \hat{H}_e. \tag{2.9}$$

It follows that

$$\hat{H}\Psi = (\hat{T}_n + \hat{v}_n)\Psi + \hat{H}_e\Psi.$$

If

$$\Psi(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e}) = \Psi_e(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e})\Psi_n(\mathbf{X}_1, \cdots, \mathbf{X}_m) \tag{2.10}$$

where Ψ_e is the electronic ground state i.e. $\hat{H}_e\Psi_e = E_0\Psi_e$ then,

$$\begin{aligned}
\hat{H}\Psi &= (\hat{T}_n + \hat{v}_n)\Psi + E_0(\mathbf{X}_1, \cdots, \mathbf{X}_m)\Psi && (2.11)\\
&= (\hat{T}_n\Psi_e)\Psi_n + \Psi_e(\hat{T}_n\Psi_n) + \Psi_e(\hat{v}_n\Psi_n) + E_0(\mathbf{X}_1, \cdots, \mathbf{X}_m)\Psi && (2.12)\\
&= (\hat{T}_n\Psi_e)\Psi_n + \Psi_e[\hat{T}_n + \hat{v}_n + E_0(\mathbf{X}_1, \cdots, \mathbf{X}_m)]\Psi_n. && (2.13)
\end{aligned}$$

The dependency of E_0 on $\mathbf{X}$ results from the presence of the nuclear potential operator in Eq. (2.8). Looking for the electronic properties of the system and keeping in mind that the mass of a nucleon is 10^3 heavier than this of an electron, one may choose the centre of the nuclei as the inert frame to localize the electrons and therefore neglect the kinetic part $\hat{T}_n\Psi_e$ in Eq. (2.13). This implies that,

$$\hat{H}\Psi = \Psi_e[\hat{T}_n + \hat{v}_n + E_0(\mathbf{X}_1, \cdots, \mathbf{X}_m)]\Psi_n.$$

If we neglect $\hat{T}_n\Psi_e$, Ψ_n turns out to be an eigenfunction of the nuclear Hamiltonian

$$\hat{H}_n = \hat{T}_n + \hat{v}_n + E_0(\mathbf{X}_1, \cdots, \mathbf{X}_m). \tag{2.14}$$

This concludes BO's assumption stated in Eq. (2.10). Alongside this approach, from the assumption of a nuclear inert frame, one may consider Eq. (2.1). Neglecting $\hat{T}_n\Psi$, Eq. (2.7) is reduced to

$$\Big(\hat{v}_n + \hat{T}_e + \hat{u} + \hat{v}_{n-e}\Big)\Psi_e(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e}) = E\Psi_e(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e}).$$

Under the assumption of fixed nuclei, the nucleon-nucleon potential is a constant and can be shifted to the right hand side so that one remains only with $\hat{T}_e + \hat{u} + \hat{v}_{n-e}$. That is,

$$\begin{aligned}
\Big(\hat{T}_e + \hat{u} + \hat{v}_{n-e}\Big)\Psi_e(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e}) &= (E - \hat{v}_n)\Psi_e(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e})\\
&= E_0(\mathbf{X}_1, \cdots, \mathbf{X}_m)\Psi_e(\mathbf{X}_1, \cdots, \mathbf{X}_m, \mathbf{x}_1, \cdots, \mathbf{x}_{n_e}).
\end{aligned}$$

From now forth and without loss of generality, let us still denote by $\hat{H}$,

$$\hat{H} = \hat{T} + \hat{u} + \hat{v}, \tag{2.15}$$

the electronic Hamiltonian where $\hat{v}$ now stands for the external potential. We are now on interested in the following Schrödinger equation:

$$\hat{H}\Psi(\mathbf{x}_1, \cdots, \mathbf{x}_{n_e}) = E\Psi(\mathbf{x}_1, \cdots, \mathbf{x}_{n_e}). \tag{2.16}$$

2.2 Hartree and Hartree-Fock Method

Though it looks simple and obviously resolvable, Eq. (2.16) is seldomly easy to be handled straightforward when the number of electrons in the system increases (albeit the BO approximation has brought down the effort that is initially needed). Only further devised simplifications can allow one to expect solving this challenging equation.

2.2.1 Hartree Method

The first steps have been taken by Hartree, Fock and Slater in the HF method. In the Hartree method, each electron is regarded as moving in a single particle self-consistent potential field created by both nuclei and electrons of the system. Henceforth, the many-electron Hartree wave function (also called a Hartree product) ϕ is the product of one-electron wave functions $\varphi_i, 1 \leq i \leq n_e$. The many-electron Hamiltonian becomes a linear combination of one-particle Hamiltonians $\hat{H}(\mathbf{x}_i)$. So, the one-electron wave functions form an orthonormal basis and are solutions of

$$\hat{H}(\mathbf{x}_i)\varphi_i = \epsilon_i\varphi_i.$$

The solutions of Eq. (2.16) are assumed to be on the form of the Hartree product:

$$\phi(\mathbf{x}_1, \cdots, \mathbf{x}_{n_e}) = \varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)\cdots\varphi_{n_e}(\mathbf{x}_{n_e}). \tag{2.17}$$

The later statement can be put on an analytical way as follows using the variational principle:

$$\left\langle \delta_i\phi \left| \hat{H} - \epsilon_i \right| \phi \right\rangle \Big|_{\phi=\phi_0} = 0 \tag{2.18}$$

where ϕ_0 corresponds to the ground state wave function. In Eq. (2.18), $\delta_i\phi$ is the state obtained after slightly varying the i^{th} single-electron wave function φ_i used to write ϕ. For instance, and throughout this thesis, the variation will affect only one of the φ_i so that we get

$$\delta_i\phi = \varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)\cdots\varphi_{i-1}(\mathbf{x}_{i-1})\delta\varphi_i(\mathbf{x}_i)\varphi_{i+1}(\mathbf{x}_{i+1})\cdots\varphi_{n_e}(\mathbf{x}_{n_e}). \tag{2.19}$$

While expanding Eq. (2.18) using Eq. (2.19), we have carried out (see Appendix A) the one particle potential

$$\hat{v}^H(\mathbf{r}_k) = \sum_{i,i\neq k}^{n_e} \langle\varphi_i^\dagger(\mathbf{x}_i)\hat{u}(\mathbf{r}_i, \mathbf{r}_k)\varphi_i(\mathbf{x}_i)\rangle_{\mathbf{r}_i} \tag{2.20}$$

$$= \sum_{i,i\neq k}^{n_e} \int \varphi_i^\dagger(\mathbf{x}_i)\hat{u}(\mathbf{r}_i, \mathbf{r}_k)\varphi_i(\mathbf{x}_i)d\mathbf{r}_i \tag{2.21}$$

which is the famous self-consistent potential field called Hartree potential. We have also worked out the single-electron Schrödinger equation

$$\Big(\hat{T}_k + \hat{v}^H(r_k) + \hat{v}(r_k)\Big)\varphi_k = \epsilon_k \varphi_k. \tag{2.22}$$

The functional

$$F^H[\varphi] = \langle \varphi^\dagger(\mathbf{x})\Big(\hat{T} + \hat{v}^H(\mathbf{r})\Big)\varphi(\mathbf{x})\rangle \tag{2.23}$$

is completely independent of any kind of information the nuclei of the system may carry. For instance, its analytical expression is the same for all sort of atomic or molecular systems with equal number of electrons. So, it is universal and it is called universal functional. Unfortunately, as pointed out by Fock and Slater, the Hartree product does not respect Pauli exclusion principle. Once the system contains more than one electron, the Hartree wave functions are no more suitable to be considered. In fact let us consider a two-electron Hartree product $\phi(\mathbf{x}_1, \mathbf{x}_2) = \varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)$. If one assumes that both electrons occupied the same one-particle wave function then, $\varphi_1 = \varphi_2 = \varphi$ and

$$\phi(\mathbf{x}_1, \mathbf{x}_2) = \varphi(\mathbf{x}_1)\varphi(\mathbf{x}_2).$$

The Hartree product does not necessary vanish and so does violate the Pauli exclusion principle.

2.2.2 Hartree-Fock Method

Slater, to clarify the approach used by Fock in addressing the drawback in the Hartree product, introduced the Slater determinant

$$\phi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_{n_e}) = \frac{1}{\sqrt{n_e!}} \det \begin{pmatrix} \varphi_1(\mathbf{x}_1) & \cdots & \varphi_{n_e}(\mathbf{x}_1) \\ \vdots & \cdots & \vdots \\ \vdots & \cdots & \vdots \\ \varphi_1(\mathbf{x}_{n_e}) & \cdots & \varphi_{n_e}(\mathbf{x}_{n_e}) \end{pmatrix} \tag{2.24}$$

which can be thought of as a generalization of the Hartree product as follows

$$\phi_H(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_{n_e}) = \det \begin{pmatrix} \varphi_1(\mathbf{x}_1) & 0 & \cdots & 0 \\ 0 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \varphi_{n_e}(\mathbf{x}_{n_e}) \end{pmatrix}.$$

Considering the Slater determinant, the expansion of Eq. (2.18) yields the Hartree-Fock equations:

$$\Big[\hat{T}_{\mathbf{r}} + \hat{v}^H(\mathbf{r}) + \hat{v}^x[\mathbf{r}, \varphi_k] + \hat{v}\Big]\varphi_k(\mathbf{x}) = \epsilon_k \varphi_k(\mathbf{x}) \tag{2.25}$$

where

$$\hat{v}^x[\mathbf{r}, \varphi_k] = \sum_{m, m\neq k}^{n_e} \varphi_m^\dagger(\mathbf{x}')\hat{u}(\mathbf{r}, \mathbf{r}')\varphi_k(\mathbf{x}')\varphi_m(\mathbf{x}) \tag{2.26}$$

is a delocalised potential because of its dependency on φ_k. It is called the exchange potential. The HF universal functional becomes

$$F^{HF}[\varphi] = \langle \varphi^\dagger(\mathbf{x})\Big(\hat{T} + \hat{v}^H(\mathbf{r}) + \hat{v}^x[\mathbf{r}, \varphi]\Big)\varphi(\mathbf{x})\rangle. \tag{2.27}$$

Though a Slater determinant is a non-correlated anti-symmetric wave function since

$$\phi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_j, \cdots, \mathbf{x}_i, \cdots, \mathbf{x}_{n_e}) = -\phi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_i, \cdots, \mathbf{x}_j, \cdots, \mathbf{x}_{n_e}),$$

their convex combinations are correlated. Thus, the solutions ψ_i of Eq. (2.16) are assumed to be convex combination of (a subset of) all possible Slater determinants ϕ_j. Henceforth, they are correlated anti-symmetric wave functions. This wave function is more plausible than the Hartree product ϕ_H. In the Hartree approach it is assumed that the i^{th} electron occupied the state φ_i. In other words, one knows exactly the position of each electron independently of the time the measurement is made. Nevertheless, it is known that electrons are indistinguishable so that they can likely occupy each of the state available. This later aspect is well captured in Eq. (2.24). As an operator, the determinant of a matrix wherein there is a column that is a linear combination of others vanishes; thus, assuming an orbital shared by two electrons yields a zero wave function. That is, the use of Slater determinants ensures the respect of the Pauli exclusion principle.

2.3 Density functional theory

As its name conveys it, Density Functional Theory aims at formulating the description of measurable observables of a given system in terms of the ground state electronic density. It began with Thomas and Fermi, was placed on a firm formal basis by Hohenberg, Kohn and Sham and has become one of the most used techniques in the field of computational materials science.

2.3.1 Thomas-Fermi method

DFT in its earlier age began with the Thomas-Fermi statement in 1927. Instead of studying the system by looking for its ground state Ψ_0, Thomas and Fermi introduced [18, 33, 34, 35] the electronic density ρ_0 as the main subject. For instance, for a system with more than two electrons, a geometrical insight into the electronic density ρ_0 (a three-dimensional variable dependent function) is obviously more efficient than the ground state wave function which involves at least six dimensional variables.

Thomas and Fermi started by considering an elementary volume $\Delta V_{\mathbf{r}}$ around the position vector $\mathbf{r}$. They hypothesised on a uniform density $\rho(\mathbf{r})$ to show that (see Appendix A.3) the kinetic energy T^{TF},

$$T^{TF} = \frac{\hbar^2}{2m_e}\left(\frac{\sqrt[3]{3^5\pi^4}}{5}\right)\int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r})^{5/3} d\mathbf{r}, \tag{2.28}$$

the coulomb interaction potential energy U^{TF},

$$U^{TF} = \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) v^{TF}(\mathbf{r}) d\mathbf{r}, \tag{2.29}$$

and the external potential energy E_v,

$$E_v = \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r},$$

are density functionals. This development allows to fully express the total energy of the system as a functional of the uniform electronic density as

$$E^{TF} = \frac{\hbar^2}{2m_e}\left(\frac{\sqrt[3]{3^5\pi^4}}{5}\right)\int_{\Delta V_{\mathbf{r}}}\rho(\mathbf{r})^{5/3}d\mathbf{r} + \int_{\Delta V_{\mathbf{r}}}\rho(\mathbf{r})v^{TF}(\mathbf{r})d\mathbf{r} + \int_{\Delta V_{\mathbf{r}}}\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \tag{2.30}$$

The functional

$$F^{TF} = \frac{\hbar^2}{2m_e}\left(\frac{\sqrt[3]{3^5\pi^4}}{5}\right)\int_{\Delta V_{\mathbf{r}}}\rho(\mathbf{r})^{5/3}d\mathbf{r} + \int_{\Delta V_{\mathbf{r}}}\rho(\mathbf{r})v^{TF}(\mathbf{r})d\mathbf{r} \tag{2.31}$$

is the TF universal functional. Since the ground state density is the one that minimizes the total energy and integrates to n_e over the coordinate space (here $\Delta V_{\mathbf{r}}$), the following equations hold:

$$\int_{\Delta V_{\mathbf{r}}}\Big[\kappa'\rho(\mathbf{r})^{2/3} + v^{TF}(\mathbf{r}) + v(\mathbf{r}) - \mu\Big]\delta\rho d\mathbf{r} = 0$$

$$\kappa'\rho_0(\mathbf{r})^{2/3} + v^{TF}(\mathbf{r}) + v(\mathbf{r}) = \mu. \tag{2.32}$$

Eq. (2.32) is the TF equation and is used to determine the ground state properties of the system. TF method reduced a lot the calculations by introducing homogeneous gases. Though F^{TF} is deduced from an homogeneous gas, it is used to locally assess inhomogeneous systems. However, the method remains a mathematical model since its universal functional is too crude to describe a natural system i.e. a non-uniform electronic density.

2.3.2 Density functional theory

Kohn together with Hohenberg and Sham have generalized the Thomas-Fermi idea of homogeneous density into an inhomogeneous density. Let us define the spin independent density

$$\rho_0(\mathbf{r}_1) = n_e \sum_{\sigma_1,\sigma_2,\cdots,\sigma_{n_e}}\int_{\mathbb{R}^3} d\mathbf{r}_2\int_{\mathbb{R}^3} d\mathbf{r}_3\cdots\int_{\mathbb{R}^3} d\mathbf{r}_{n_e}\left\langle\Psi_0(\mathbf{x}_1,\cdots,\mathbf{x}_{n_e})\right|\Psi_0(\mathbf{x}_1,\cdots,\mathbf{x}_{n_e})\rangle.$$

*

Inversely, any trial wave function Ψ becomes an implicit functional of the many-electron density ρ. The expectation value of the Hamiltonian gives

$$E = \left\langle\Psi\left|\hat{H}\right|\Psi\right\rangle \tag{2.33}$$

$$= \langle\Psi\left|\hat{T}+\hat{u}\right|\Psi\rangle + \langle\Psi\left|\hat{v}\right|\Psi\rangle \tag{2.34}$$

$$= \langle\Psi\left|\hat{T}+\hat{u}\right|\Psi\rangle + \int\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}. \tag{2.35}$$

Since the two operators $\hat{T}$ and $\hat{u}$ are both ρ-independent i.e. fixed, the first term of the right hand side, denoted by F, is an implicit functional of ρ while the second term is an explicit functional. So, the energy

$$E[\rho] = F[\rho] + \int\rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \tag{2.36}$$

is also a functional of the electronic density. The functional F does not take into account where the external potential v arises from; it is therefore a universal functional. Once F is well established in terms of ρ and the external potential is given, it will serve to determine the ground or excited state properties of the system. The fact that the density determines the wave function induces a functional

dependency of any observable measurement on the density. From this observation, Hohenberg and Kohn (HK) moved forwards to establish two pinpoint theorems that underpin the concept of DFT for non-degenerate ground states [36]. HK's theorem was improved and generalized for degenerate ground states later. They state that the density is uniquely determined by the external potential and that the energy of the system, apart from being a functional of the density, reaches its minimum exactly at the ground state density. Indeed, let us consider two external potentials $\hat{v}$ and $\hat{v}'$ with their corresponding Hamiltonians $\hat{H}$ and $\hat{H}'$ and degenerate ground state wave functions $\Psi_{0,i}$ and $\Psi'_{0,i}$. The two Hamiltonians are related by the expression $\hat{H}' = \hat{H} + (\hat{v}' - \hat{v})$. The wave functions

$$\Psi_0 = \sum_{i \in I} \alpha_i \Psi_{0,i}$$

and

$$\Psi'_0 = \sum_{i \in I'} \alpha'_i \Psi'_{0,i},$$

where $\alpha_i, \alpha'_i \in \mathbb{C}$ and

$$\sum_i |\alpha_i|^2 = \sum_i |\alpha'_i|^2 = 1,$$

are ground state wave functions of $\hat{H}$ and $\hat{H}'$ respectively. Because of the degeneracy, it is necessary to introduce some new sets. First, let $\mathcal{V}$ include all external potentials that differ by more than a constant; $\mathcal{S}_v$ and $\mathcal{D}_v$ be the sets of linear combinations of the associated ground state wave functions and densities of v; and $\mathcal{S} = \cup_v \mathcal{S}_v$ and $\mathcal{D} = \cup_v \mathcal{D}_v$. If one assumes that the external potentials differ by more than a constant and that $\rho'_0 = \rho_0$ then the following hold

$$\begin{aligned}
E'_0 &= \left\langle \Psi'_0 \middle| \hat{H}' \middle| \Psi'_0 \right\rangle \\
&= \left\langle \Psi'_0 \middle| \hat{H} \middle| \Psi'_0 \right\rangle + \int (v'(\mathbf{r}) - v(\mathbf{r}))\rho_0(\mathbf{r}) d\mathbf{r} \\
&= \sum_i |\alpha'_i|^2 \left\langle \Psi'_{0,i} \middle| \hat{H} \middle| \Psi'_{0,i} \right\rangle + \int (v'(\mathbf{r}) - v(\mathbf{r}))\rho_0(\mathbf{r}) d\mathbf{r} \\
&> \sum_i |\alpha'_i|^2 E_0 + \int (v'(\mathbf{r}) - v(\mathbf{r}))\rho_0(\mathbf{r}) d\mathbf{r}
\end{aligned}$$

because $\Psi'_{0,i}$ are not eigenfunctions of $\hat{H}$. In other words,

$$E'_0 > E_0 + \int (v'(\mathbf{r}) - v(\mathbf{r}))\rho_0(\mathbf{r}) d\mathbf{r}. \tag{2.37}$$

Eq. (2.37) can be rewritten by permuting the symbol $'$ to obtain

$$E_0 > E'_0 + \int (v(\mathbf{r}) - v'(\mathbf{r}))\rho_0(\mathbf{r}) d\mathbf{r}. \tag{2.38}$$

Eq. (2.37) and Eq. (2.38) together sum up to give

$$E'_0 + E_0 > E'_0 + E_0$$

which is contradictory. Thus, it is not possible to get the same density (or $\mathcal{D}_v$) from two potentials that do not differ by a constant. The proof for the non-degenerate wave function case emanates from the choice of $\alpha_0 = \alpha'_0 = 1$ and $\alpha_i = \alpha'_i = 0$ for $i \neq 0$. This concludes the proof of the HK's theorem for both degenerate and non-degenerate ground states. The attempt to look for a density that minimizes

the energy demands the use of $\frac{\delta E}{\delta \rho}$ that mathematically required some topological structure over $\mathcal{D}$ or an extended set. In general, the energy can be evaluated for any arbitrary density as its functional. However, does a trial density result from an external potential? The answer is no. Those densities that correspond to a potential belong to $\mathcal{D}$ and are called v-representable. $\mathcal{D}$ is not a compact set that will contain an infinitesimal variation of its elements. Thus, Levy in his work assumes a more relax set that contains densities coming from any plausible n_e-electron wave functions (degenerate or not and no necessary v-representable) called n_e-representable wave functions. In the Levy constrained search, the energy becomes

$$\begin{aligned} E[\rho_0] &= \min_{\rho} \left\{ \min_{\Psi \to \rho} \left\{ \left\langle \Psi[\rho] \left| \hat{T} + \hat{u} \right| \Psi[\rho] \right\rangle + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\} \right\} \\ &= \min_{\rho} \left\{ \min_{\Psi \to \rho} \left\{ \left\langle \Psi[\rho] \left| \hat{T} + \hat{u} \right| \Psi[\rho] \right\rangle \right\} + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\} \\ &= \min_{\rho} \left\{ F^L[\rho] + \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \right\} \end{aligned} \tag{2.39}$$

where $F^L[\rho] = \min_{\Psi \to \rho} \left\{ \left\langle \Psi[\rho] \left| \hat{T} + \hat{u} \right| \Psi[\rho] \right\rangle \right\}$. The search for ρ_0 using the variation of the energy with respect to n_e-representable density accordingly to the statement of Eq. (2.39) is permitted now.

2.3.3 Hartree-Fock-like equations: Kohn-Sham equations

Hohenberg and Kohn rigorously settled the formal basis of DFT and the existence of the universal functional F^{HK}. They did not offer a method to implement DFT. The next step was to think about methods and schemes to implement DFT. The Hartree-Fock scheme offered a suggestion which Kohn and Sham used to develop a practical implementation of DFT. First, let us consider the Hamiltonian $\hat{H}_{KS}$ of a noninteracting system that has the same ground state density as $\hat{H}$. In their derivation Hohenberg and Kohn did not use the properties of the non interaction potential though DFT can be applied to noninteracting systems as well. The noninteracting universal functional is nothing else than the noninteracting kinetic functional T^{KS}. The external potential, v^{KS}, of the fictitious noninteracting particle system is called the Kohn-Sham potential. The KS ground state wave function Φ_0 is solution of

$$\left(\hat{T}^{KS} + \hat{v}^{KS} \right) \Phi_i = E_i^{KS} \Phi_i, \tag{2.40}$$

which yields

$$E_0^{KS} = T^{KS}[\rho_0] + \int \rho_0(\mathbf{r}) v^{KS}(\mathbf{r}) d\mathbf{r}.$$

The ground state density minimizes the density functional

$$E^{KS}[\rho] = T^{KS}[\rho] + \int \rho(\mathbf{r}) v^{KS}(\mathbf{r}) d\mathbf{r}$$

with the constrain

$$\int \rho(\mathbf{r}) d\mathbf{r} = n_e$$

in such away that the Lagrange multiplier μ' satisfies

$$\mu' = \frac{dT^{KS}}{d\rho}[\rho_0] + v^{KS}[\rho_0]. \tag{2.41}$$

The many-particle KS ground state wave-function will be a sum of Slater determinants which are constructed from single particle orbitals. We can formulate a Hartree-Fock like energy by taking the expectation value of the interaction potential with respect to the KS ground state wave function. The resulting expression can be expressed as a sum of two terms, the Hartree energy, $E^H[\rho]$ and the exchange energy $E^x[\rho]$:

$$\langle \Phi \left| \hat{u} \right| \Phi \rangle = E^H \left[\rho\right] + E^x \left[\rho\right]$$

where

$$E^H[\rho] = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

and $E^x\left[\rho\right]$ has the form of the Hartree-Fock exchange energy, but expressed in terms of the KS orbitals.

The interacting system ground state energy $E\left[\rho\right]$, can be written as

$$\begin{aligned} E\left[\rho\right] &= \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \langle \Psi \left| \hat{u} \right| \Psi \rangle + \langle \rho v \rangle \\ &= \left\langle \Phi \left| \hat{T} \right| \Phi \right\rangle + \left(\left\langle \Psi \left| \hat{T} + \hat{u} \right| \Psi \right\rangle - \left\langle \Phi \left| \hat{T} + \hat{u} \right| \Phi \right\rangle \right) + \langle \Phi \left| \hat{u} \right| \Phi \rangle + \langle \rho v \rangle \\ &= \left\langle \Phi \left| \hat{T} \right| \Phi \right\rangle + E^c\left[\rho\right] + E^x\left[\rho\right] + E^H\left[\rho\right] + \langle \rho v \rangle \end{aligned} \tag{2.42}$$

where the correlation energy $E^c\left[\rho\right]$, is defined as

$$E^c\left[\rho\right] = \left\langle \Psi \left| \hat{T} + \hat{u} \right| \Psi \right\rangle - \left\langle \Phi \left| \hat{T} + \hat{u} \right| \Phi \right\rangle. \tag{2.43}$$

It is common to combine the exchange and correlation energies and we will write $E^c\left[\rho\right] + E^x\left[\rho\right] = E^{xc}\left[\rho\right]$ when required. The universal Hohenberg-Kohn functional $F^L[\rho]$ can therefore be decomposed as

$$\begin{aligned} F^L[\rho] &= \left\langle \Psi \left| \hat{T} \right| \Psi \right\rangle + \langle \Psi \left| \hat{u} \right| \Psi \rangle \\ &= T^{KS}[\rho] + E^{xc}\left[\rho\right] + E^H\left[\rho\right]. \end{aligned} \tag{2.44}$$

It follows from Eq. (2.44) that the energy of the interacting system can be written

$$E[\rho] = T^{KS}[\rho] + E^H[\rho] + E^{xc}[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}$$

and, since $E\left[\rho\right]$ is minimised at the ground state density ρ_0,

$$\mu = \frac{dT^{KS}}{d\rho}[\rho_0] + \int \frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{dE^{xc}}{d\rho}[\rho_0] + v[\rho_0], \tag{2.45}$$

where μ is a Lagrange multiplier that comes from the requirement that the particle number is constrained. Therefore,

$$v^{KS}[\rho_0] = (\mu' - \mu) + \left(\int \frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \frac{dE^{xc}}{d\rho}[\rho_0] + v[\rho_0] \right).$$

Hence, after defining

$$v^H[\rho(\mathbf{r})] = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \tag{2.46}$$

(details on how to derive the Hartree potential is given in Section 2.4.2) and

$$v^{xc}[\rho(\mathbf{r})] = \frac{dE^{xc}}{d\rho}, \tag{2.47}$$

the definition of the KS potential and the KS equations (up to a constant shift $\mu' - \mu$) follows as

$$v^{KS}[\rho_0] = v^{H}[\rho_0] + v^{xc}[\rho_0] + v[\rho_0] \tag{2.48}$$

with

$$\left(\hat{T}_i + \hat{v}^{KS}(\mathbf{r}_i)\right)\varphi_i = \epsilon_i \varphi_i. \tag{2.49}$$

These last equations help to extract the interacting density from a self-consistent resolution (based on v^{KS}) of the noninteracting system. Thus, inhomogeneous densities can be obtained and used to assess the accuracy of universal functional approximations or simply E^{xc} approximations.

2.3.4 The exchange-correlation potential

DFT provides a full formalism on how to get the ground state energy and density of any system but left us without any mention of how to obtain the exchange correlation potential. This led researchers to ponder the question of how to express or to approximate the missing linchpin of the theory. Over decades, substantial and hefty approximations have been achieved.

Local density approximation

The local density approximation [1, 2, 21] is an admirable approximation based on homogeneous systems. The ground state density is therefore uniform and the knowledge of the density is assumed to accurately establish a local exchange-correlation energy density $\epsilon^{xc}(\rho(r))$ which integrates to E^{xc}. That is

$$\begin{aligned} E^{xc}[\rho] &= \int_r \epsilon^{xc}(\rho(r))dr \\ &= \sum_{i=1}^{n_e} \epsilon^{xc}(\rho_i). \end{aligned}$$

In return, $\epsilon^{xc}(\rho(r)) = \dfrac{\partial}{\partial\rho}E^{xc}$ and leads to the single-particle Schrödinger equations

$$(-\frac{1}{2}\nabla_i^2 + v^H + \epsilon^{xc} + v)\varphi_i = \epsilon_i\varphi_i.$$

It is noteworthy that the dependence of the exchange-correlation energy density on the uniform electronic density demands to analytically establish ϵ^{xc}. An approach known as Bethe ansatz [37, 38, 39, 40, 41] gives an exact expression of ϵ^{xc} (Eq. (4.4)) for one dimensional Hubbard models (see Section 3.2.1). The form of ϵ^{xc} that is devised may then be used as reference for inhomogeneous system E^{xc} calculation. LDA showed some shortcomings in calculation of bang gap of materials [42, 43, 44]. When consideration for spin is at stake, $\rho_\uparrow$ and $\rho_\downarrow$ become the variable of ϵ^{xc} and the approximation is named LSD or local spin density.

Derivative of local density approximation: Gradient approximation and hybrids

In general, the exchange-correlation energy density can be written not only as functional of ρ but also of $|\nabla\rho|$, $\nabla^2\rho$ and many other functional of ρ. In such case the expression for LDA is the first order term in the Taylor expansion of ϵ^{xc} with respect to $|\nabla\rho|$ or $\nabla^2\rho$ for slowly varying ground state density. The choice and the manipulation of the power series and its variables are intently motivated by known properties of the density functionals that one aims to incorporate into the approximation. Despite their growing number, the different approximations are grouped into few categories mainly the generalized gradient approximation (GGA) [45, 46], the meta-GGAs (MGGA) and the hybrid-GGAs (HGGA) [27, 28, 29] with $\epsilon^{xc}(\rho, |\nabla\rho|)$, $\epsilon^{xc}(\rho, |\nabla\rho|, \nabla^2\rho)$ and $\epsilon^{xc}(\rho, |\nabla\rho|, \nabla^2\rho, \epsilon^x_{exact})$ [47, 48] respectively and where ϵ^x_{exact} is an exact exchange energy density.

The sake of approximate density functional has led to the development of several approximations. The one that outperformed for some particular type of problems may be outperformed for other types. So, the approximations are designed to accurately address a range of properties. For instance to study thermodynamic or electronic structure, Perdew–Burke–Ernzerhof (PBE) functional is among the privileged ones [47] though it fails to estimate charge transfer excitation energies.

2.4 Ensemble DFT

2.4.1 Canonical ensemble

Ensemble DFT [49, 50] is the branch of DFT that is taken into account by physics to probe a system of fractional N particle number. For a system that exchanges electrons and energy with an infinitely large and distant reservoir, the average number of electrons within the system can be fractional. To describe this, one may go beyond the simple ground state density to use the ensemble ground state density ρ_0^N. While exchanging electrons, the real system can be found in a range of n_e-electron systems with possible degenerate ground states $\Psi_i^{n_e}$ and its corresponding electron density $\rho_i^{n_e}$ for $i \in I_{n_e} \subset \mathbb{N}$. The superscript n_e of $\rho_i^{n_e}$ involves the result $\int_{\mathbb{R}^3} \rho_i^{n_e}(\mathbf{r})d\mathbf{r} = n_e$. For such n_e-electron systems, let $p_{n_e,i}$ be the probability to find the real system in the state $\Psi_i^{n_e}$. Obviously,

$$\sum_{n_e}\sum_{i\in I} p_{n_e,i} = 1. \tag{2.50}$$

A well defined operator (matrix) able to consider at once (and perhaps all the past and future of) those n_e-electron systems is

$$\hat{\Gamma} = \sum_{n_e}\sum_{i} |\Psi_i^{n_e}\rangle\, p_{n_e,i}\, \langle\Psi_i^{n_e}| \tag{2.51}$$

or for simplicity

$$\hat{\Gamma} = \sum_{i} |\Psi_i\rangle\, p_i\, \langle\Psi_i| \tag{2.52}$$

and is called canonical ensemble. Eq. (2.50) implies that $Tr(\hat{\Gamma}) = 1$ where Tr means trace. Recall that Ψ_i are the eigenfunctions of the Hamiltonian $\hat{H} = \hat{T} + \hat{u} + \hat{v}$. The expectation value of any

observable $\hat{O}$ is equal to the trace of $\hat{\Gamma}\hat{O}$. That is

$$\begin{aligned}\langle\hat{O}\rangle &= \sum_i p_i \left\langle \Psi_i \left| \hat{O} \right| \Psi_i \right\rangle \\ &= Tr\Big(\hat{\Gamma}\hat{O}\Big).\end{aligned}$$

Thus, the ground ensemble density and energy are defined by

$$\rho(\mathbf{r}) = \sum_i p_i \rho_i(\mathbf{r})$$

and

$$E = \sum_i p_i E_i.$$

Let us denote by $\hat{\Gamma}_\rho$ the canonical ensemble that yields the density ρ. ρ equals ρ_0 at zero temperature. One can figure out several canonical ensembles that yield the same electronic density. For instance, one may think of varying the outcome probabilities in those cases. The Variational principle is therefore over all ensembles $\hat{\Gamma}_\rho$.

2.4.2 KS potential property recovered from the canonical ensemble

It is convenient to work out the (canonical) ensemble $\hat{\Gamma}_{\rho^{n_e^+}}$ of a system with fractional particle number n_e^+ which is between n_e and $n_e + 1$. Fortunately, data suggests that the ground state energies of the Hamiltonian of such opened system satisfy the so-called convexity condition [50, 51] as listed below,

$$2E_{n_e} \leq \Big(E_{n_e+1} + E_{n_e-1}\Big). \tag{2.53}$$

Hence, for $\alpha = n_e^+ - n_e$ one may interpolate the ensemble $\hat{\Gamma}_{\rho^{n_e^+}}$ as follows

$$\hat{\Gamma}_{\rho^{n_e^+}} = (1-\alpha)\sum_i \left|\Psi_i^{n_e}\right\rangle p_i \left\langle \Psi_i^{n_e}\right| + \alpha\sum_i \left|\Psi_i^{n_e+1}\right\rangle p_i \left\langle \Psi_i^{n_e+1}\right|, \tag{2.54}$$

$$= (1-\alpha)\hat{\Gamma}_{\rho^{n_e}} + \alpha\hat{\Gamma}_{\rho^{n_e+1}}. \tag{2.55}$$

So, in particular one has

$$\rho^{n_e^+} = (1-\alpha)\rho^{n_e} + \alpha\rho^{n_e+1}$$

and

$$E_{n_e^+} = (1-\alpha)E_{n_e} + \alpha E_{n_e+1}. \tag{2.56}$$

Let us replace α by $n_e^+ - n_e$ in Eq. (2.56) and thereafter take the derivative of the energy $E_{n_e^+}$ with respect to n_e^+. Substituting α by $n_e^+ - n_e$,

$$\text{Eq. (2.56)} \Longrightarrow E_{n_e^+} = (1 + n_e - n_e^+)E_{n_e} + (n_e^+ - n_e)E_{n_e+1}.$$

Now, the derivative gives

$$\frac{\partial E_{n_e^+}}{\partial n_e^+} = E_{n_e+1} - E_{n_e}. \tag{2.57}$$

In other words, the derivative of the total energy is constant in the interval $[n_e, n_e + 1]$. So, if one takes n_e^- in $[n_e - 1, n_e]$ rather than considering it in $[n_e, n_e + 1]$, one must straightforwardly obtain

$$\frac{\partial E_{n_e^-}}{\partial n_e^-} = E_{n_e} - E_{n_e-1}. \tag{2.58}$$

In general, $\frac{\partial E_N}{\partial N}$ is known as the chemical potential, μ_N, of the interacting N-electron system and in particular,

$$E_{n_e} - E_{n_e+1} = A(n_e) \text{ is the electron affinity}$$

and

$$E_{n_e-1} - E_{n_e} = I(n_e) \text{ is the ionization potential.}$$

Eqs. (2.57) and (2.58) together with Eq. (2.53) result into

$$\mu_{n_e}^- = \lim_{n_e^- \to n_e} \frac{\partial E_{n_e^-}}{\partial n_e^-} \leq \lim_{n_e^+ \to n_e} \frac{\partial E_{n_e^+}}{\partial n_e^+} = \mu_{n_e}^+. \tag{2.59}$$

Data show that $I(n_e) - A(n_e)$ is zero for metals whereas it is strictly positive for semiconductors and insulators. This affects directly either the effective Kohn-Sham or the exchange-correlation potential as proved in the following lines. Firstly, let us consider the ensemble version of the Hohenberg-Kohn second theorem that states

$$\begin{aligned}
E[\rho^N] &= \min_{\hat{\Gamma}_{\rho^N}} \Big\{ Tr(\hat{\Gamma}_{\rho^N}(\hat{T} + \hat{u} + \hat{v})) \Big\} \\
&= \min_{\hat{\Gamma}_{\rho^N}} \Big\{ Tr(\hat{\Gamma}_{\rho^N}(\hat{T} + \hat{u})) + Tr(\hat{\Gamma}_{\rho^N}\hat{v}) \Big\} \\
&= \min_{\hat{\Gamma}_{\rho^N}} \left\{ Tr(\hat{\Gamma}_{\rho^N}(\hat{T} + \hat{u})) + \int_{\mathbb{R}^3} \rho^N(\mathbf{r})\hat{v}(\mathbf{r})d\mathbf{r} \right\} \\
&= \min_{\hat{\Gamma}_{\rho^N}} \Big\{ Tr(\hat{\Gamma}_{\rho^N}(\hat{T} + \hat{u})) \Big\} + \int_{\mathbb{R}^3} \rho^N(\mathbf{r})\hat{v}(\mathbf{r})d\mathbf{r} \\
&= F[\rho^N] + E_v[\rho^N]
\end{aligned}$$

and

$$\begin{aligned}
E[\rho_0^N] &= \min_{\rho^N} \big\{ F[\rho^N] + E_v[\rho^N] \big\} \\
&= F[\rho_0^N] + E_v[\rho_0^N].
\end{aligned}$$

This means

$$\frac{\delta E}{\delta \rho} = \frac{\delta F}{\delta \rho} + v$$

where

$$v = \frac{\delta E_v}{\delta \rho}$$

is independent of ρ^N; $F[\rho^N]$ is a universal canonical functional. On the other hand, the variational principle upon the N-electron interacting functional energy says

$$\frac{\delta}{\delta\{\rho(\mathbf{r}), \mu_N\}} \Big[\Big\langle \Psi[\rho] \Big| \hat{H} \Big| \Psi[\rho] \Big\rangle + \mu_N \Big(N - \int_{\mathbb{R}^3} \rho(\mathbf{r})d\mathbf{r} \Big) \Big] = 0.$$

It turns out that

$$\frac{\delta F}{\delta \rho^N}[\rho_0^N] + v = \mu_N$$

since

$$\frac{\delta}{\delta \mu_N}\Big[\mu_N\Big(N - \int_{\mathbb{R}^3} \rho(\mathbf{r}) d\mathbf{r}\Big)\Big] = 0$$

implies

$$\int_{\mathbb{R}^3} \rho(\mathbf{r}) d\mathbf{r} = N.$$

Let us consider the KS universal functional energy

$$F^{KS}[\rho^N] = \Big[T^{KS} + E^H + E^{xc}\Big][\rho^N].$$

With

$$E^H[\rho^N] = \frac{1}{2}\int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho^N(r)\rho^N(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}',$$

the variational of the Hartree energy is

$$\begin{aligned}\delta E_H[\rho^N] &= \frac{1}{2}\Big[\int \delta\rho^N(\mathbf{r}') \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho^N(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \int \delta\rho^N(\mathbf{r}) \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho^N(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}' d\mathbf{r}\Big] \\ &= \int_{R^3} \delta\rho^N(\mathbf{r}) d\mathbf{r} \Big(\int_{\mathbb{R}^3} \frac{\rho^N(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'\Big)\end{aligned}$$

that is

$$v^H[\rho^N] = \int_{\mathbb{R}^3} \frac{\rho^N(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \tag{2.60}$$

Therefore,

$$\frac{\delta}{\delta \rho^N}\Big(T^{KS} + E^{xc}\Big)[\rho_0^N] + v^H[\rho_0^N] = \mu_N. \tag{2.61}$$

According to Eq. (2.55) the density is continuous at integer particle number; so is $v^H[\rho^N]$. Therefore,

$$\lim_{n_e^- \to n_e} \frac{\delta}{\delta \rho^{n_e^-}}\Big(T^{KS} + E^{xc}\Big)[\rho_0^{n_e^-}] \leq \lim_{n_e^+ \to n_e} \frac{\delta}{\delta \rho^{n_e^+}}\Big(T^{KS} + E^{xc}\Big)[\rho_0^{n_e^+}] \tag{2.62}$$

which is the cornerstone of the well known spatially independent discontinuity of the KS or the XC potential at integer particle numbers. Another issue coming from Eq. (2.62) is whether $\frac{\delta T^{KS}}{\delta \rho^N}$ or

$$v^{xc} = \frac{\delta E_{xc}}{\delta \rho^N}$$

is a discontinuous function. The discontinuity in the Kohn-Sham potential was first discussed by Perdew et al. in 1982 [51]. Eq. (2.62) shows that the functional derivative ot the kinetic energy plus exchange correlation energy can have a spatially independent discontinuity in its functional derivative at integer particle numbers. According to the first Hohenberg-Kohn theorem the groundstate charge density determines the groundstate potential to within a constant. Applied to the Kohn-Sham system at integer particle numbers, it implies, since the groundstate density is continuous with respect to the particle number, that the KS potential as an integer particle number is approached from above can

differ from the KS potential as the same integer particle number is approached from below, only by a spatially independent constant. This means that the KS potential can have a spatially independent discontinuity at integer particle numbers. The discontinuity in the KS potential is discussed in [50, 52, 51], for example, but this simple conclusion, based on the Hohenberg-Kohn theorem has not been investigated. The consequence is that both the KS potential and the functional derivative of the kinetic energy have spatially independent discontinuities at integer particle numbers.

Taking into account the behaviour of the KS potential we can now derive an expression for the discontinuity of the functional derivative of the KS kinetic energy. Let v_+^{KS} and v_-^{KS} be the KS potentials when one approaches respectively from above or below the n_e-particle system. The shift in the potentials is denoted by λ i.e.

$$\lambda = v_+^{KS} - v_-^{KS}. \tag{2.63}$$

If φ_i are the solutions to the KS equations:

$$-\frac{1}{2}\nabla^2\varphi_i + v^{KS}\varphi_i = \epsilon_i\varphi_i \tag{2.64}$$

then, for an arbitrary N

$$\rho_0^N(\mathbf{r}) = \sum_{i\in\mathbb{N}}\theta_i|\varphi_i|^2(\mathbf{r}) \text{ where } \begin{cases} \theta_i = 1 \text{ if } 1 \le i \le n_e \\ 0 \le \theta_i < 1 \text{ otherwise.} \end{cases}$$

Therefore,

$$\nabla^2\rho_0^N = \sum_{i\in\mathbb{N}}\theta_i\Big(2\nabla\varphi_i^\dagger\nabla\varphi_i + \varphi_i^\dagger\nabla^2\varphi_i + (\nabla^2\varphi_i^\dagger)\varphi_i\Big) \tag{2.65}$$

which implies

$$\sum_{i\in\mathbb{N}}\theta_i\Big(\varphi_i^\dagger\nabla^2\varphi_i + (\nabla^2\varphi_i^\dagger)\varphi_i\Big) = -\nabla^2\rho_0^N + \sum_{i\in\mathbb{N}}\theta_i\Big(2\nabla\varphi_i^\dagger\nabla\varphi_i\Big).$$

Eq. (2.64) yields

$$\begin{aligned} -\frac{1}{2}\sum_{i\in\mathbb{N}}\theta_i\varphi_i^\dagger\nabla^2\varphi_i + v^{KS}\sum_{i\in\mathbb{N}}\theta_i|\varphi_i|^2 &= \sum_{i\in\mathbb{N}}\theta_i\epsilon_i|\varphi_i|^2 \\ -\frac{1}{2}\sum_{i\in\mathbb{N}}\theta_i\varphi_i^\dagger\nabla^2\varphi_i + (\mu_N - \frac{\delta T^{KS}}{\delta\rho^N}[\rho_0^N])\sum_{i\in\mathbb{N}}\theta_i|\varphi_i|^2 &= \sum_{i\in\mathbb{N}}\theta_i\epsilon_i|\varphi_i|^2 \\ -\frac{1}{2}\sum_{i\in\mathbb{N}}\theta_i\varphi_i^\dagger\nabla^2\varphi_i - \rho_0^N\frac{\delta T^{KS}}{\delta\rho^N}[\rho_0^N] &= -\sum_{i\in\mathbb{N}}\theta_i(\mu_N - \epsilon_i^N)|\varphi_i|^2. \end{aligned} \tag{2.66}$$

Both Eq. (2.65) and Eq. (2.66) lead to

$$\frac{\delta T^{KS}}{\delta\rho^N}[\rho_0^N] = \frac{1}{4\rho_0^N}\nabla^2\rho_0^N - \frac{1}{2\rho_0^N}\sum_{i\in\mathbb{N}}\theta_i\Big(\nabla\varphi_i^\dagger\nabla\varphi_i\Big) + \frac{1}{\rho_0^N}\sum_{i\in\mathbb{N}}\theta_i(\mu_N - \epsilon_i^N)|\varphi_i|^2;$$

in particular,

$$\frac{\delta T^{KS}}{\delta\rho^{n_e^+}}[\rho_0^{n_e^+}] = \frac{1}{4\rho_0^{n_e^+}}\nabla^2\rho_0^{n_e^+} - \frac{1}{2\rho_0^{n_e^+}}\sum_{i=1}^{n_e+1}\theta_i\Big(\nabla\varphi_i^\dagger\nabla\varphi_i\Big) + \frac{1}{\rho_0^{n_e^+}}\sum_{i=1}^{n_e+1}\theta_i(\mu_{n_e^+} - \epsilon_i^+)|\varphi_i|^2$$

and

$$\frac{\delta T^{KS}}{\delta\rho^{n_e^-}}[\rho_0^{n_e^-}] = \frac{1}{4\rho_0^{n_e^-}}\nabla^2\rho_0^{n_e^-} - \frac{1}{2\rho_0^{n_e^-}}\sum_{i=1}^{n_e}\theta_i\Big(\nabla\varphi_i^\dagger\nabla\varphi_i\Big) + \frac{1}{\rho_0^{n_e^-}}\sum_{i=1}^{n_e}\theta_i(\mu_{n_e^-} - \epsilon_i^-)|\varphi_i|^2.$$

Hence, with $\Big[\frac{\delta T^{KS}}{\delta\rho}\Big]^{+}[\rho_0^{n_e}] = \lim\limits_{n_e^{+}\to n_e} \frac{\delta T^{KS}}{\delta\rho^{n_e^{+}}}[\rho_0^{n_e^{+}}]$ and $\Big[\frac{\delta T^{KS}}{\delta\rho}\Big]^{-}[\rho_0^{n_e}] = \lim\limits_{n_e^{-}\to n_e} \frac{\delta T^{KS}}{\delta\rho^{n_e^{-}}}[\rho_0^{n_e^{-}}]$,

$$\begin{aligned}
\Big(\Big[\frac{\delta T^{KS}}{\delta\rho}\Big]^{+} - \Big[\frac{\delta T^{KS}}{\delta\rho}\Big]^{-}\Big)[\rho_0^{n_e}] &= \frac{1}{\rho_0^{n_e}}\sum_{i=1}^{n_e}\theta_i(\mu_{n_e}^{+} - \epsilon_i^{+})|\varphi_i|^2 - \frac{1}{\rho_0^{n_e}}\sum_{i=1}^{n_e}\theta_i(\mu_{n_e}^{-} - \epsilon_i^{-})|\varphi_i|^2 \\
&= \frac{1}{\rho_0^{n_e}}\sum_{i=1}^{n_e}\theta_i(\epsilon_{n_e+1}^{+} - \epsilon_i^{-})|\varphi_i|^2 - \frac{1}{\rho_0^{n_e}}\sum_{i=1}^{n_e}\theta_i(\epsilon_{n_e}^{-} - \epsilon_i^{-})|\varphi_i|^2 \\
&= \frac{1}{\rho_0^{n_e}}\sum_{i=1}^{n_e}\theta_i(\epsilon_{n_e+1}^{+} - \epsilon_{n_e}^{-})|\varphi_i|^2 \\
\Big(\Big[\frac{\delta T^{KS}}{\delta\rho}\Big]^{+} - \Big[\frac{\delta T^{KS}}{\delta\rho}\Big]^{-}\Big)[\rho_0^{n_e}] &= \epsilon_{n_e+1}^{+} - \epsilon_{n_e}^{-}. \qquad (2.67)
\end{aligned}$$

On the other hand,

$$E^{KS}(n_e)^{\pm} = (T^{KS})^{\pm}[\rho_0^{n_e}] + E_{v^{KS}}^{\pm}$$

and Eq. (2.33) bring us to

$$\lambda n_e = (T^{KS})^{+}[\rho_0^{n_e}] - (T^{KS})^{-}[\rho_0^{n_e}] + \lambda n_e.$$

That is

$$(T^{KS})^{+}[\rho_0^{n_e}] = (T^{KS})^{-}[\rho_0^{n_e}]. \qquad (2.68)$$

It is clear that the convexity condition occasions a shift or a discontinuity in the KS potential (Eq. (2.63)) though T^{KS} is a continuous function (Eq. (2.68)); whereas Eq. (2.67) shows that the functional derivative of the KS kinetic energy at integer particle numbers may or may not exhibit a discontinuity since $\epsilon_{n_e+1}^{+} - \epsilon_{n_e}^{-}$ is zero for opened systems and different of zero otherwise. In this thesis we are interested in studying the discontinuity of the KS potential and devised approximations that preserve the existence of the gaps.

Chapter 3

Lattice density functional theory

3.1 Second quantization

3.1.1 Fermion Fock space

Contrary to classical particles, quantum mechanics particles (bosons and fermions) are indistinguishable. This leads to wave functions that highlight only the different occupied states by the quantum particles instead of their individual position. In case of L site lattice of one electron, the normalized state $|i\sigma\rangle$ stands for a delta function representing a spin σ particle localised at site i. Eigenstates for a one particle system are therefore superposition of the delta functions (see Appendix B.2); that is,

$$\varphi_{i\sigma} = \sum_{j=1}^{L} \beta_{i_j} \, |i_j\sigma\rangle$$

are eigenstates. The set $\{ \varphi_{i\sigma} \mid 1 \leq i \leq L, \sigma = \uparrow, \downarrow \}$[1] generates a single-electron complex Hilbert space ($\mathcal{H}$) since it forms a vector space equipped with the scalar product $\langle \bullet | \bullet \rangle$ that induces a norm on the space. The states of two electron lattice system belong to the second tensor power $\mathcal{H}^{\otimes 2}$ of $\mathcal{H}$. Each term of the product carries information on a single electron. Furthermore, for n_e-electron system, the states are antisymmetric tensors of $\mathcal{H}^{\otimes n_e}$. They are also called Fock states because they are built up with basis elements which are made of the same number (n_e) of electrons. Indeed, the n_e^{th} tensor powers of $\mathcal{H}$ can be sum up to construct the Fock space, [53]

$$\mathcal{F} = \bigoplus_{n_e=0}^{2L} \mathcal{H}^{\otimes n_e}.$$

Among the antisymmetric Fock states, there are the pure states that are factorizable as follows

$$\phi = \sum_i b_{i_1} \varphi_{i_1\sigma_i} \otimes \sum_i b_{i_2} \varphi_{i_2\sigma_i} \otimes \cdots \otimes \sum_i b_{i_{n_e}} \varphi_{i_{n_e}\sigma_i}. \tag{3.1}$$

Otherwise, they are called entangled states. Indeed, while expanding the tensor product in Eq (3.1), one readily comes across with tensor power terms like

$$b_{i_{\theta(1)} i_{\theta(2)} \cdots i_{\theta(n_e)}} \varphi_{i_{\theta(1)}\sigma_{\theta(1)}} \varphi_{i_{\theta(2)}\sigma_{\theta(2)}} \cdots \varphi_{i_{\theta(n_e)}\sigma_{\theta(n_e)}}$$

[1] The basis of $\varphi_{i\sigma}$ is only used here for demonstration purpose. For numerical calculations, the Hamiltonians are diagonalized over the basis of delta functions $|i\sigma\rangle$

where θ is an arbitrary permutation, $1 \leq i_j \leq L$, $i_j = i_k$ implies that $\sigma_j \neq \sigma_k$ and may occur only once in the product. In other words,

$$\phi = \sum_{(i_1, i_2, \cdots, i_{n_e})} \sum_{\theta} b_{i_{\theta(1)} i_{\theta(2)} \cdots i_{\theta(n_e)}} \bigotimes_{j=1}^{n_e} \varphi_{i_{\theta(j)} \sigma_{\theta(j)}}.$$

The antisymmetry condition affects as well the components which satisfy

$$b_{i_{\theta(1)} i_{\theta(2)} \cdots i_{\theta(n_e)}} = (-1)^{\epsilon_\theta} b_{i_1 i_2 \cdots i_{n_e}}$$

where ϵ_θ is the number of time θ permutes two elements. Finally, one may consider the normalized antisymmetric states

$$\phi_i = \sum_{\theta} \frac{(-1)^{\epsilon_\theta}}{\sqrt{n_e!}} \bigotimes_{j=1}^{n_e} \varphi_{i_{\theta(j)} \sigma_{\theta(j)}} \tag{3.2}$$

in order to rewrite ϕ as follows

$$\phi = \sum_i b_i \phi_i.$$

3.1.2 Creation and annihilation operators

To further simplify the complexity of performing a general expansion of tensor powers, the creation and annihilation operators [54, 55] are introduced. Let us consider the sub vector space $\mathcal{H}_-^{\otimes n_e}$ of all the antisymmetric states ϕ_i of $\mathcal{H}^{\otimes n_e}$ defined in Eq (3.2). The linear operator

$$\begin{aligned} \hat{C}^\dagger_{k\sigma} : \quad \mathcal{H}_-^{\otimes n_e} \quad &\mapsto \quad \mathcal{H}_-^{\otimes n_e+1} \\ \phi_i(1, 2, \cdots, n_e) \quad &\to \quad \phi_i(1, 2, \cdots, n_e, n_e+1) = \sum_{\theta} \frac{(-1)^{\epsilon_\theta}}{\sqrt{(n_e+1)!}} \bigotimes_{j=1}^{n_e+1} \varphi_{i_{\theta(j)} \sigma_{\theta(j)}} \end{aligned}$$

is called the creation operator and satisfies

$$\{\hat{C}^\dagger_{k\sigma}, \hat{C}^\dagger_{k'\sigma'}\} = \hat{C}^\dagger_{k\sigma} \hat{C}^\dagger_{k'\sigma'} + \hat{C}^\dagger_{k'\sigma'} \hat{C}^\dagger_{k\sigma} = 0 \tag{3.3}$$

and for all θ there exists j such that $\left| i_{\theta(j)} \sigma_{\theta(j)} \right\rangle = |k\sigma\rangle$. It basically creates a spin σ electron at site k. A glance at Eq. (3.3) shows that $\hat{C}^\dagger_{k\sigma} \hat{C}^\dagger_{k\sigma} = 0$ and this manifests the Pauli's exclusion principle. The Hilbert space for an empty lattice is the complex space $\mathbb{C}$. A state in $\mathbb{C}$ is linear to $|\rangle$; the so called vacuum space. The creation operator maps then the zero-electron Hilbert space $\mathbb{C} = \mathcal{H}^{\otimes 0}$ into a single electron space $\mathcal{H}^{\otimes 1}$ i.e. $\hat{C}^\dagger_{k\sigma} |\rangle = |k\sigma\rangle$. Thereon, a repeat action of n_e different creation operators on the vacuum lead to the basis elements

$$\hat{C}^\dagger_{i_1\sigma_1} \hat{C}^\dagger_{i_2\sigma_2} \cdots \hat{C}^\dagger_{i_{n_e}\sigma_{n_e}} |\rangle$$

of $\mathcal{H}_-^{\otimes n_e}$ so that one can choose

$$\phi_i = \hat{C}^\dagger_{i_1\uparrow} \hat{C}^\dagger_{i_2\uparrow} \cdots \hat{C}^\dagger_{i_{n_\uparrow}\uparrow} \hat{C}^\dagger_{i_{(n_\uparrow+1)}\downarrow} \hat{C}^\dagger_{i_{(n_\uparrow+2)}\downarrow} \cdots \hat{C}^\dagger_{i_{n_e}\downarrow} |\rangle \tag{3.4}$$

to represent the basis elements. Let us stress on the use of the subscript $n_\uparrow$ to denote the number of up-spin electrons carried by ϕ_i. The inverse of the creation operator is the annihilation operator $\hat{C}$ defined as follows

$$\begin{aligned}\hat{C}_{k\sigma}: \quad \mathcal{H}_{-}^{\otimes n_e} &\mapsto \mathcal{H}_{-}^{\otimes n_e-1} \\ \phi_i(1,2,\cdots,n_e-1,n_e) &\to \phi_i(1,2,\cdots,n_e-1) = \sum_{\theta} \frac{(-1)^{\epsilon_\theta}}{\sqrt{(n_e-1)!}} \bigotimes_{j=1}^{n_e-1} \varphi_{i_{\theta(j)}\sigma_{\theta(j)}}\end{aligned}$$

which satisfies

$$\{\hat{C}_{k\sigma}, \hat{C}_{k'\sigma'}\} = 0 \tag{3.5}$$

and for all θ, there is not any j such that $\left|i_{\theta(j)}\sigma_{\theta(j)}\right\rangle = |k\sigma\rangle$. All state of $\mathcal{H}_{-}^{\otimes n_e}$ that does not involve the single state $|k\sigma\rangle$ will be totally quenched (mapped into 0) by $\hat{C}_{k\sigma}$ otherwise only the single state $|k\sigma\rangle$ is removed. The combination of the two operators lead to the following relationship

$$\{\hat{C}_{k\sigma}^{\dagger}, \hat{C}_{k'\sigma'}\} = \delta_{kk'}\delta_{\sigma\sigma'}.$$

These two operators have been involved into building useful and relevant operators. In quantum mechanics, operators are aimed to be hermitian. Such operators are called observable since their eigenvalues are real and can be obtained experimentally. Among them are

$$\begin{aligned}\hat{n}_{i\sigma} &= \hat{C}_{i\sigma}^{\dagger}\hat{C}_{i\sigma}, \text{ the on-site spin } \sigma \text{ particle number operator} \\ \hat{n}_{\sigma} &= \sum_i \hat{n}_{i\sigma}, \text{ the spin } \sigma \text{ particle number operator} \\ \hat{n}_i &= \sum_{\sigma} \hat{n}_{i\sigma}, \text{ the on-site particle number operator} \\ \hat{n}_e &= \sum_{i,\sigma} \hat{n}_i, \text{ the total particle number operator} \\ \hat{S}_z &= \frac{1}{2}\sum_i (\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow}), \text{ the spin number operator}\end{aligned}$$

3.2 One dimensional Hamiltonian model

In physics, an Hamiltonian is mainly used to describe and to investigate some particular properties of a system. For a lattice system, it serves for instance in studying the quantum mechanical motion (tunnelling or hopping), the coulomb interaction of electrons and also the external potential or magnetic field. There are various Hamiltonians, however, regarding the aims of the investigation one has to make a concise choice. We chose the Hubbard Hamiltonian to describe our system because it bears enough features that are sometime difficult to be retrieved from the complex system itself; also, it is no more a simple mathematical model since it can be realized experimentally using wave laser light fields [56].

3.2.1 Hubbard Hamiltonian

The Hubbard model is named after John Hubbard who has published a series of papers [57, 58, 59, 60, 61] in this regards. Meanwhile, Gutzwiller [62] and Kanamori [63] came out independently with the same model whence the trio Hubbard-Gutzwiller-Kanamori model was used in the past.

The Hubbard Hamiltonian is introduced to model crystalline materials. This makes the nucleon-nucleon and the nucleon-electron interaction potentials to be periodic potentials with the same period as the lattice. The application of the BO approximation with the change, $P^2 = -\hbar^2\nabla^2$,

$\mathcal{U}(\mathbf{x}_i, \mathbf{x}_j) = \frac{e^2}{4\pi\epsilon} \frac{1}{|\mathbf{r}_j - \mathbf{r}_i|}$ and $\mathcal{V}(\mathbf{x}_i) = -\frac{e^2}{4\pi\epsilon} \sum_{j=1}^{m} \frac{Z_j}{|\mathbf{R}_j - \mathbf{r}_i|}$ reduces the Hamiltonian of Eq. (2.1) into

$$H = \sum_{i=1}^{n_e} \frac{P_i^2}{2m_e} + \sum_{1 \leq i < j \leq n_e} \mathcal{U}(\mathbf{x}_i, \mathbf{x}_j) + \sum_{i=1}^{n_e} \mathcal{V}(\mathbf{x}_i).$$

The coulomb potential, though it is a two-electron potential, is to complex to facilitate a mean field approximation. Therefore, one needs to come out with a simpler two-electron potential. This can be achieved by considering an auxiliary potential $\mathcal{V}'$ [30]. The addition and removal of $\sum_{i=1}^{n_e} \mathcal{V}'(\mathbf{x}_i)$ from H, yield:

$$H = \sum_{i=1}^{n_e} \frac{P_i^2}{2m_e} + \sum_{1 \leq i < j \leq n_e} \mathcal{U}(\mathbf{x}_i, \mathbf{x}_j) - \sum_{i=1}^{n_e} \mathcal{V}'(\mathbf{x}_i) + \sum_{i=1}^{n_e} \left[\mathcal{V}(\mathbf{x}_i) + \mathcal{V}'(\mathbf{x}_i)\right].$$

Let us define the one-electron potential $v'(\mathbf{x}_i) = \mathcal{V}(\mathbf{x}_i) + \mathcal{V}'(\mathbf{x}_i)$ and the two-electron potential $u(\mathbf{x}_i, \mathbf{x}_j) = \mathcal{U}(\mathbf{x}_i, \mathbf{x}_j) + \frac{1}{(n_e - 1)} \left[\mathcal{V}'(\mathbf{x}_i) + \mathcal{V}'(\mathbf{x}_j)\right]$. The sum of the elements $\sum_{j \neq i} \mathcal{V}'(\mathbf{x}_j)$, $1 \leq i \leq n_e$, gives $(n_e - 1) \sum_{i=1}^{n_e} \mathcal{V}'(\mathbf{x}_i)$. Therefore,

$$\begin{aligned}
\sum_{i=1}^{n_e} \mathcal{V}'(\mathbf{x}_i) &= \frac{2}{n_e - 1} \sum_{1 \leq i < j \leq n_e} \mathcal{V}'(\mathbf{x}_j) \\
&= \frac{1}{n_e - 1} \left[\sum_{1 \leq i < j \leq n_e} \mathcal{V}'(\mathbf{x}_j) + \sum_{1 \leq i < j \leq n_e} \mathcal{V}'(\mathbf{x}_j) \right] \\
&= \frac{1}{(n_e - 1)} \left[\sum_{1 \leq i < j \leq n_e} \mathcal{V}'(\mathbf{x}_i) + \sum_{1 \leq i < j \leq n_e} \mathcal{V}'(\mathbf{x}_j) \right]
\end{aligned} \tag{3.6}$$

implies

$$\begin{aligned}
\sum_{1 \leq i < j \leq n_e} \mathcal{U}(\mathbf{x}_i, \mathbf{x}_j) - \sum_{i=1}^{n_e} \mathcal{V}'(\mathbf{x}_i) &= \sum_{1 \leq i < j \leq n_e} \left(\mathcal{U}(\mathbf{x}_i, \mathbf{x}_j) + \frac{1}{(n_e - 1)} \left[\mathcal{V}'(\mathbf{x}_i) + \mathcal{V}'(\mathbf{x}_j)\right] \right) \\
&= \sum_{1 \leq i < j \leq n_e} u(\mathbf{x}_i, \mathbf{x}_j)
\end{aligned}$$

and

$$H = \sum_{i=1}^{n_e} H(\mathbf{x}_i) + \sum_{1 \leq i < j \leq n_e} u(\mathbf{x}_i, \mathbf{x}_j). \tag{3.7}$$

We recall that $H(\mathbf{x}_i) = \frac{P_i^2}{2m_e} + v'(\mathbf{x}_i)$ is the one-electron Hamiltonian with eigenfunctions and eigenenergies $\varphi_{\alpha\mathbf{k}}$ and $\epsilon_{\alpha\mathbf{k}}$ respectively. α represents the band index while $\mathbf{k}$ is the crystal momentum that runs over the first Brillouin zone (BZ). The periodicity of the lattice constrains $\varphi_{\alpha\mathbf{k}}$ to be periodic functions. The eigenfunctions are therefore Bloch functions [64, 56] and so can be written as

$$\varphi_{\alpha\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}.\mathbf{r}} u_{\alpha\mathbf{k}}(\mathbf{r}).$$

They form an orthonormal basis and span the one-electron system. For lattice systems, it is more convenient to make use of maximally localized wave functions. Since Bloch functions are periodic, they can be decomposed into Fourier series. If, over the lattice vectors $\mathbf{R}_j$, the Fourier coefficients are $\xi_{\alpha\mathbf{R}_j}$ with $\xi_{\alpha\mathbf{R}_j}(\mathbf{r}) = \xi_\alpha(\mathbf{r} - \mathbf{R}_j)$, then

$$\varphi_{\alpha\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{m}} \sum_{\mathbf{R}_j} e^{i\mathbf{k}.\mathbf{R}_j} \xi_{\alpha\mathbf{R}_j}(\mathbf{r}).$$

$\xi_{\alpha\mathbf{R}_j}$ are localized functions around the lattice points; they are named Wannier functions. Inversely, one can Fourier transform the Wannier functions over the first BZ to get the Bloch eigenfunctions. That is,

$$\xi_{\alpha\mathbf{R}_j}(\mathbf{r}) = \frac{1}{\sqrt{m}} \sum_{\mathbf{k}\in BZ} e^{-i\mathbf{k}.\mathbf{R}_j} \varphi_{\alpha\mathbf{k}}(\mathbf{r}).$$

A spin σ electron in the Wannier (respectively Bloch) state can be acted on by the creation, $\hat{C}^\dagger_{j\sigma,\alpha}$ ($\hat{C}^\dagger_{\mathbf{k}\sigma,\alpha}$), or the annihilation, $\hat{C}_{j\sigma,\alpha}$ ($\hat{C}_{\mathbf{k}\sigma,\alpha}$) operator. In general, one defines the spin σ creation field operator as follows:

$$\hat{\psi}^\dagger_\sigma(\mathbf{r}) = \sum_{j,\alpha} \xi^*_{\alpha\mathbf{R}_j}(\mathbf{r}) \hat{C}^\dagger_{j\sigma,\alpha}. \tag{3.8}$$

The definition of the annihilation field operator results from Eq. (3.8). Let us now second quantized the Hamiltonian. Eq. (3.7) becomes,

$$\begin{aligned} H &= \sum_{\sigma=\uparrow,\downarrow} \int d^3\mathbf{r} \hat{\psi}^\dagger_\sigma(\mathbf{r}) H(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) + \frac{1}{2} \sum_{\sigma,\sigma'=\uparrow,\downarrow} \int d^3\mathbf{r} d^3\mathbf{r}' \hat{\psi}^\dagger_\sigma(\mathbf{r}) \hat{\psi}^\dagger_{\sigma'}(\mathbf{r}') u(\mathbf{r},\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_\sigma(\mathbf{r}) \\ &= \sum_\sigma \sum_{\alpha\alpha',ij} t^{\alpha\alpha'}_{ij,\sigma} \hat{C}^\dagger_{i\sigma,\alpha} \hat{C}_{j\sigma,\alpha'} + \frac{1}{2} \sum_{\sigma\sigma'} \sum_{\alpha\alpha'\beta\beta',ijkl} u^{\alpha\alpha'\beta\beta'}_{ijkl} \hat{C}^\dagger_{i\sigma,\alpha} \hat{C}^\dagger_{j\sigma,\alpha'} \hat{C}_{k\sigma,\beta'} \hat{C}_{l\sigma,\beta} \end{aligned}$$

where

$$\begin{aligned} t^{\alpha\alpha'}_{ij,\sigma} &= \int d^3\mathbf{r} \xi^*_{\alpha\mathbf{R}_i}(\mathbf{r}) H(\mathbf{r}) \xi_{\alpha'\mathbf{R}_j}(\mathbf{r}) \\ &= \frac{1}{m} \sum_{\mathbf{k}\in BZ} e^{i\mathbf{k}.(\mathbf{R}_i - \mathbf{R}_j)} \int d^3\mathbf{r} \varphi^*_{\alpha\mathbf{k}}(\mathbf{r} - \mathbf{R}_i) H(\mathbf{r}) \varphi_{\alpha'\mathbf{k}}(\mathbf{r} - \mathbf{R}_j) \\ &= \frac{\delta_{\alpha\alpha'}}{m} \sum_{\mathbf{k}\in BZ} e^{i\mathbf{k}.(\mathbf{R}_i - \mathbf{R}_j)} \epsilon_{\alpha\mathbf{k}} \end{aligned}$$

and

$$u^{\alpha\alpha'\beta\beta'}_{ijkl} = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \xi^*_{\alpha\mathbf{R}_i}(\mathbf{r}) \xi^*_{\alpha'\mathbf{R}_j}(\mathbf{r}') u^{\alpha\alpha'\beta\beta'}_{ijkl}(\mathbf{r},\mathbf{r}') \xi_{\beta'\mathbf{R}_k}(\mathbf{r}') \xi_{\beta\mathbf{R}_l}(\mathbf{r}). \tag{3.9}$$

The simplest form of the Hubbard Hamiltonian is reached by only allowing the nearest neighbour hopping without the on-site term. This means that one has adopted the following setting:

$$t_{ij,\sigma} = -t\delta_{|i-j|-1}$$

and

$$u^{\alpha\alpha'\beta\beta'}_{ijkl} = u_0 \delta_{\alpha\alpha'} \delta_{\alpha'\beta} \delta_{\beta\beta'} \delta_{ij} \delta_{jk} \delta_{kl}.$$

The parameter t is in unit energy and quantifies the energy released by an electron that hops from one site to the closest one. On its simplest form, the Hubbard Hamiltonian for an homogeneous system is as follows:

$$\hat{H} = -t \sum_{<i,j>,\sigma} \hat{C}^\dagger_{j\sigma} \hat{C}_{i\sigma} + u_0 \sum_{i=1}^{n_e} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}.$$

For inhomogeneous system, an external potential field $\hat{v}$ has to be added. In case of a spin-dependent potential, one has

$$\hat{v} = \sum_{i\sigma} v_{i\sigma} \hat{n}_{i\sigma};$$

otherwise, $v_{i\sigma} = v_i$ for both spins.

3.2.2 Some properties of the Hubbard Hamiltonian ground state wave function

The Hubbard Hamiltonian does commute with the spin-number operator $\hat{S}_z$ since it commutes with $\hat{n}_{i\sigma}$. So, the Hubbard Hamiltonian does not change the number of up and down spin particles when acting on a basis function, and therefore it is block diagonal in the basis functions with $N_\uparrow$ up-spin and $N_\downarrow$ down-spin particles. We note that for the ground state,

$$\varsigma_0 = \sum_m h(m)\phi_m,$$

of the Hubbard Hamiltonians (for dependent or independent particles) the discrete function h has a constant sign (see Section 6.2.1 for details) for positive hopping term t. This property holds for all t in general as it is proved from Eq. (6.5) to Eq. (6.7) and stated in [30]. We numerically investigate the constant sign property of h via simulations in order to confront the theory and the numerical results.

The Hubbard Hamiltonian depends on the hopping term, the interacting term and the external potential. Any change in these parameters induces a change in the ground state wave function. We look at this with respect to each parameter while arranging the basis functions ϕ_m according to the occurrence of the electron spins at the different sites. While varying the parameter u_0 between -10 and 10, we select a flat external potential and set the hopping term to one. Figure 3.1 plots the function h against the corresponding basis function indices m for all values of u_0. A glance at the patterns draw upon the different colour, marker and line styles shows that the respective components are of the same sign and may be equal to zero. Moreover, when one magnifies enough the left hand side of Figure 3.1 in Figure 3.2, it appears that the components are only close to zero. Here, we only plot the graph for four electrons because it is the worst case in terms of the components being close enough

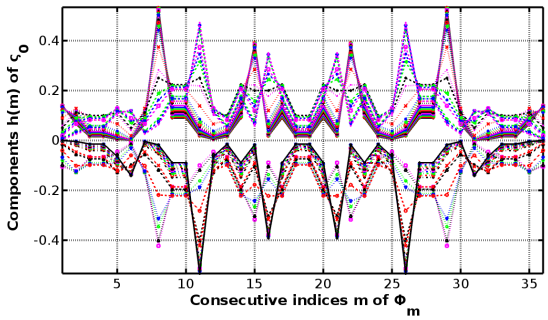


Figure 3.1: The components $h(m)$ of ς_0 against the basis vector ϕ_m indices m for forty one values of u_0 spreads evenly over the range $[-10, 10]$ and for $v = (1, 1, 1, 1)$.

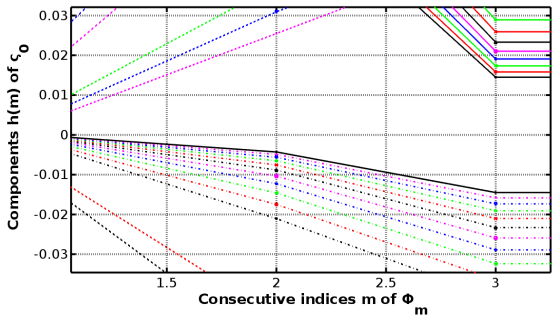


Figure 3.2: Zoom in the left end of Figure 3.1.

to zero. We then vary the external potential whether arbitrary using a uniform distribution or flat. We notice that the results are still the same (even when we change the lattice site number). Likewise, instead of varying the u_0 term, we evenly spread the hopping term t over the range $[1, 20]$ and replot h. The three graphs showed in Figures 3.3, 3.4 and 3.5 stress on the constant sign of the components. For the different figures above, the external potential varies for all of them except its geometry that is sometime the same. This means that, the way the potential affects the components is inherent to these figures. So, the sign of the components does not differ as well. The same observations hold for the components $h(m)$ of the noninteracting Hubbard Hamiltonian ground state wave function.

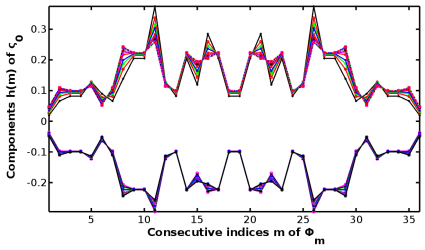


Figure 3.3: The components $h(m)$ of ς_0 against the basis vector ϕ_m indices m for forty one values of t spreads evenly over the range $[1, 20]$ and for v flat.

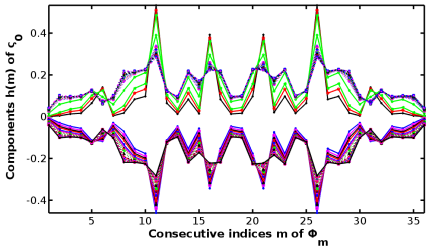


Figure 3.4: The components $h(m)$ of ς_0 against the basis vector ϕ_m indices m for forty one values of t spreads evenly over the range $[1, 20]$ and for v symmetric.

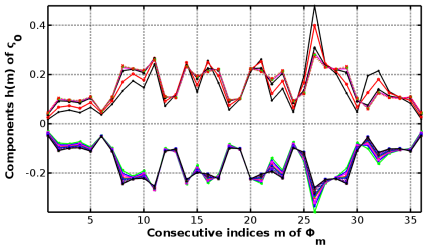


Figure 3.5: The components $h(m)$ of ς_0 against the basis vector ϕ_m indices m for forty one values of t spreads evenly over the range $[1, 20]$ and for v arbitrary.

3.2.3 Derivatives of the Hubbard Hamiltonian

Notwithstanding its simplicity, the model can be used to analyse electronic properties as well as ferromagnetism and antiferromagnetism properties and metal-insulator transition of strongly correlated or tight binding systems. Indeed, the double occupation can induce an attraction or repulsion whether u_0 is negative or positive. For strong attraction ($u_0 \to -\infty$) the system increasingly tends to allow only double occupations and so becomes antiferromagnetic [65]. Conversely, it becomes ferromagnetic for strong repulsion. The $t-J$ Hubbard model [66, 67] arises to especially address this. Other prominent derivatives of the Hubbard model are the Boson-Hubbard (for bosonic system) [68, 69, 70] and the Boson-Fermi-Hubbard model (for mixture system of bosons and fermions) and the Jaynes-Cummings-Hubbard model (for photons) [71, 72].

3.3 Density functional theory on a finite one dimensional lattice system

KSDFT [2] was originally derived for a realistic system and thereafter, regarding the interest in simplified systems, it was adapted to lattice systems in general. The main objective behind KSDFT (see Section 2.3.3) is the sake of an external potential of a fictitious noninteracting system whose electronic density is accurately equal to the electronic density of the interacting system. Since the KS system is noninteracting, any electron-electron interaction term in the Hamiltonian used to describe the system must be removed. In our case this implies $u_0 = 0$ which results in

$$\hat{H}^{KS} = \hat{T} + \hat{v}^{KS}. \tag{3.10}$$

It is worthwhile to relate how to work out the KS potential.

3.3.1 Kohn-Sham potential for realistic systems

In KSDFT one is interested in ways to figure out the KS potential of the fictitious noninteracting system. Hohenberg in [73] has given a convenient way to perform this. Assuming that the density functional E^{xc} has been established, for instance the form given in Eq. (4.4), one:

1. starts with a trial-density ρ_0,

2. works out the XC potential according to Eq. (2.47),

3. computes v^{KS} from Eq. (2.48),

4. solves the KS equation Eq. (2.40) in order to extract the ground state wave function Φ_0 and to recalculate ρ_0.

This loop is repeated until self-consistency on the density is achieved. Consequently, one expects the the approximate and the exact density to be the same.

3.3.2 An exact Kohn-Sham scheme on a lattice for spin independent KS potential

As it was said, one needs to match the density of the two systems. Any kind of information one can get on the interacting density is therefore capital. However, for small electronic systems, it is usually possible to obtain the exact density by diagonalizing the interacting Hamiltonian describing lattice systems. Knowing the exact site-occupation density $\{\rho_{0,i}\}$ it is easier to constrain the iterative density sequence $\left(\rho_i^{(k)}\right)_{k\in\mathbb{N}}$ to converge on the exact one. Therefore, one can access the exact KS potential. The following flowchart pictures in Figure 3.6 the algorithm needed to construct the spin independent KS potential. However, the KS potential is unique up to a constant shift. This necessitates extra

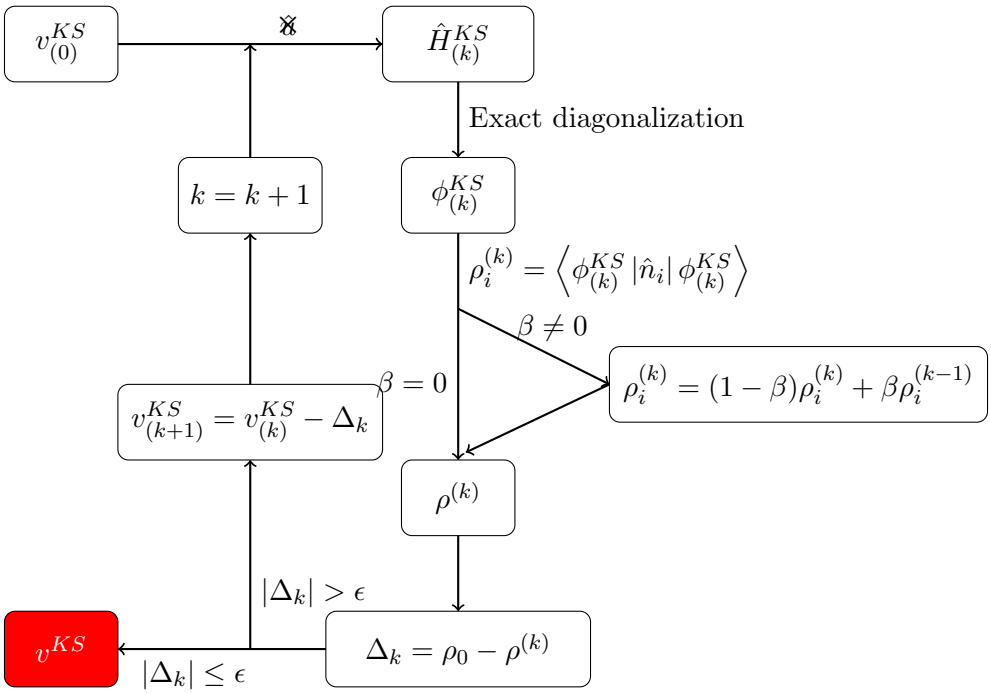


Figure 3.6: Algorithm for KS scheme.

works to converge all the outcomes into a unique potential which is indeed the KS potential. This can be done by using the chemical potential μ and the highest occupied molecular orbit or simply the n_e^{th} eigenenergy of the single particle KS Hamiltonian. This choice corresponds to considering the ionization potential

$$I = E(n_e - 1) - E(n_e)$$

to set the chemical potential. We are going to use the ionization potential henceforth. To clarify the process of determining a unique KS potential, let us consider the single particle KS Hamiltonian with an effective potential $v^{eff} = v^{KS} + c$ and its $2n_e$ eigenenergies ϵ_i. Here c is a constant included for generality since the Kohn-Sham potential is unique to within a constant. We have

$$\hat{H}^{eff}\varphi_i = \epsilon_i^{eff}\varphi_i \qquad \Longrightarrow \qquad \hat{T}_i\varphi_i + \hat{v}^{eff}\varphi_i = \epsilon_i^{eff}\varphi_i \tag{3.11}$$

$$\Longrightarrow \qquad \hat{T}_i\varphi_i + (\hat{v}^{KS} + c)\varphi_i = \epsilon_i^{eff}\varphi_i \tag{3.12}$$

$$\Longrightarrow \qquad \hat{T}_i\varphi_i + \hat{v}^{KS}\varphi_i = (\epsilon_i^{eff} - c)\varphi_i \tag{3.13}$$

$$\Longrightarrow \qquad \hat{T}_i\varphi_{n_e} + \hat{v}^{KS}\varphi_{n_e} = (\epsilon_{n_e}^{eff} - c)\varphi_{n_e} \text{ for } i = n_e. \tag{3.14}$$

It is known that ionization potential is also equal to $E^{KS}(n_e - 1) - E^{KS}(n_e)$; furthermore, being the total energy of a noninteracting system,

$$E^{KS}(n_e) = \sum_{i=1}^{n_e} \epsilon_i$$

leads to

$$\mu(n_e) = \epsilon_{n_e}.$$

Hence, Eq. (3.14) implies

$$c = \epsilon_{n_e}^{eff} - \mu(n_e). \tag{3.15}$$

This algorithm as detailed above is designed for a system of integer particle number. For fractional particle number, one needs to input the ensemble ground state density of the interacting system and repeatedly computes the ensemble KS density from the KS effective potential till a self-consistent solution and works out the KS potential. This is to say, once $v^{eff}(N)$ is known, the KS Hamiltonians for n_e and $n_e + 1$ electron systems are used to calculate the corresponding KS ground state wave functions $\Phi[n_e, v^{eff}(N)]$ and $\Phi[n_e + 1, v^{eff}(N)]$. Thereafter they serve to obtain $\rho[n_e, v^{eff}(N)]$ and $\rho[n_e + 1, v^{eff}(N)]$ which yield $\rho(N)$. Let us remind that the chemical potential is constant between consecutive integer particle numbers and only $\epsilon_{n_e}^{\text{eff}}$ will be varying in Eq. (3.15) with respect to $v^{eff}(N)$. Just like the energy, the potential can be split into

$$v^{KS} = v^H + v^{xc} + v$$

in general; wherein v^{xc} can be written as

$$v^{xc} = v^x + v^c.$$

From the need to define the "Hartree plus exchange energy"that we came across with, we have opted for the following reconstruction

$$v^{KS} = v^{Hx} + v^c + v. \tag{3.16}$$

Chapter 4

Density functional theory on a lattice: Particle number dependence of the exchange-correlation potential

4.1 Abstract

In Kohn-Sham Density Functional Theory, the interacting system is mapped onto a fictitious independent particle system. In an ensemble continuous particle number formulation the exchange-correlation contribution to the potential of the independent particle system has a discontinuity as a function of particle number at integer particle numbers [49, 50, 52, 51]. This discontinuity is equal to the difference between the fundamental gap of the interacting system and the independent particle system. As the exchange-correlation depends on the Kohn-Sham potential, we numerically investigate the exact Kohn-Sham potential as a function of particle number (either integer or fractional) for a finite dimensional Hubbard model [74] and compare the exact results to a local density approximation to the exchange-correlation functional.

We focus, in Section 4.2, on the fundamentals of Lattice-DFT [27]. In Section 4.3 the numerical approaches we used to probe the effective Kohn-Sham potential in terms of the number of electrons in the lattice using an ensemble DFT formalism are discussed. The corresponding results followed by their analysis are presented in Section 4.4. A thorough summary is included in Section 4.5.

4.2 Background

From here on N represents the number of sites of a finite one-dimensional Hubbard model, n_e is an integer number of electrons in the lattice whereas J is a fractional number of electrons. In the ensemble version of DFT fractional particle numbers J are well defined [49]. The simplest ensemble formulation arises when

$$E_0(n_e) - E_0(n_e + 1) = A,$$

the electron affinity, is less or equal to

$$E_0(n_e - 1) - E_0(n_e) = I,$$

the ionization potential. If this condition, the so-called convexity condition [50, 51], is satisfied, the energy for fractional particle numbers

$$J = (1-\alpha)n_e + \alpha(n_e+1)$$

or simply

$$J = n_e + \alpha,$$

interpolates linearly between integer particle numbers:

$$E(J) = (1-\alpha)E(n_e) + \alpha E(n_e+1).$$

In a similar way the ensemble ground density $\rho(J)$ interpolates linearly between integer particle numbers as

$$\rho(J) = (1-\alpha)\rho(n_e) + \alpha\rho(n_e+1).$$

The chemical potential,

$$\mu = \frac{\delta E(J)}{\delta n_e} \tag{4.1}$$

and the functional derivative of $E(J)$ with respect to the charge density, can therefore have a discontinuity at integer particle numbers. Depending on whether $J \geq n_e$ or $J \leq n_e$, $\mu = E(n_e+1) - E(n_e)$ or $\mu = E(n_e) - E(n_e-1)$, respectively.
We adopt the linear chain single band Hubbard Model to describe the physics on a lattice. For an external site potential $v_{i\sigma}$, the Hamiltonian is given by

$$\hat{H} = \sum_{1\leq i,j\leq N,\sigma} t_{ij}\hat{C}^\dagger_{j\sigma}\hat{C}_{i\sigma} + \sum_{1\leq i\leq N} u_i n_{i\uparrow}n_{i\downarrow} + \sum_{1\leq i\leq N,\sigma} v_{i\sigma}n_{i\sigma}. \tag{4.2}$$

Here σ is the electron spin and $\hat{C}^\dagger_{i\sigma}$ and $\hat{C}_{i\sigma}$ are respectively the Fermi creation and annihilation operators acting on spin σ electrons on site i or on the left or right vacuum. Finally, we denote by $n_{i\sigma}$ the operator $\hat{C}^\dagger_{i\sigma}\hat{C}_{i\sigma}$. The hopping matrix [74]

$$\left(t_{ij} = \left\langle \phi_j \left| -\frac{\hbar^2}{2m}\nabla^2 \right| \phi_i \right\rangle\right)_{1\leq i,j\leq N}$$

conveys the same idea of motion of particles in a general system. For simplicity, we limited the hopping amplitude up to the first neighbour on the lattice and fix them to $-t$. This means $t_{ij} = -t\delta_{(i\pm1)j}$. The on-site coulomb repulsion is carried by u_i and reflects the Hartree-Fock potential. We fixed the repulsion term to a constant u and only considered spinless external potentials ($v_{i\sigma} = v_i$). With the resulting Hamiltonian

$$\begin{aligned}\hat{H} = -t\sum_\sigma \Big[\hat{C}^\dagger_{2\sigma}\hat{C}_{1\sigma} + \sum_{i=2}^{N-1}\left(\hat{C}^\dagger_{(i-1)\sigma}\hat{C}_{i\sigma} + \hat{C}^\dagger_{(i+1)\sigma}\hat{C}_{i\sigma}\right) + \hat{C}^\dagger_{(N-1)\sigma}\hat{C}_{N\sigma}\Big] + u\sum_{1\leq i\leq N} n_{i\uparrow}n_{i\downarrow} \\ + \sum_{1\leq i\leq N,\sigma} v_i n_{i\sigma}\end{aligned} \tag{4.3}$$

we solved the finite chain Hubbard Model using Exact Diagonalization. This works well for small systems, but even for a few tenths of sites in the model, the size of the matrix makes exact diagonalization a challenge. The noninteracting, or KS system, is addressed in the Hubbard model by setting the on-site coulomb potential ($u_i = 0$) and replacing the onsite potential v_i, by the KS potential $v_{ks,i}$.

4.3 Method

We start by solving the finite interacting Hubbard model exactly and determine the ground state density. Then, starting with a guess for the KS potential, we self-consistently determine the KS-potential that yields the same density as the corresponding interacting system. This procedure determines the KS-potential to within a constant only, since potentials that differ by a constant yield the same density. However, the highest occupied KS single particle energy ϵ_{max} must satisfy

$$\mu(J, v) = \epsilon_{max}(v^{KS}),$$

where $\mu(J, v)$ is the chemical potential of the interacting J-particle system with external potential v [51]. This condition determines the KS-potential uniquely.
For comparison, we follow reference [32] and define a local density approximation (LDA) for an infinite homogeneous lattice system: the site ground state; Hartree and kinetic energies are approximated by

$$e(t, u, n_i) = \begin{cases} \frac{-2t\beta(t,u)}{\pi} \sin\left(\frac{\pi}{\beta(t,u)} n_i\right) \text{ if } n_i \leq 1 \\ \frac{-2t\beta(t,u)}{\pi} \sin\left(\frac{\pi}{\beta(t,u)}(2 - n_i)\right) + u(n_i - 1) \text{ otherwise }, \end{cases} \tag{4.4}$$

$$e_H = \frac{u}{4} n_i^2 \qquad \text{and} \qquad e_T = e(t, 0, n_i). \tag{4.5}$$

where β is the solution of

$$-\frac{2t\beta}{\pi} \sin\left(\frac{\pi}{\beta}\right) = -4t \int_0^\infty dx \frac{J_0(x) J_1(x)}{x(1 + exp(x\frac{u}{2t}))}.$$

With

$$V_{KS,i}^{LDA} = \frac{\delta}{\delta n}(e - e_T)\Big|_{n=n_i},$$

we can easily evaluate the KS potential for a given density.

4.4 Results and analysis

Let us consider a 5 site lattice with a constant potential for our application. This corresponds to a infinite potential square well. We set the on-site coulomb potential u to 2 and the hopping term t to 1 in arbitrary units. In Figure 4.1 results for the exact KS potential are shown as a function of particle number. Figure 4.2 shows results for the LDA. There are spatially independent jumps in the exact KS potential whenever the particle number passes through an integer as can clearly be seen in Figure 4.3. The LDA potential is continuous as a function of particle number as shown in Figure. 4.2. There is a rapid change in the LDA KS-potential near $J = 5$, at half band filling. This is a result of the discontinuity in the derivative of the energy of the infinite homogeneous Hubbard model at half filling (see Eq. 4.4) and is unrelated to the underlying properties of DFT. We note that, not surprisingly, both the exact and the LDA KS-potentials follow the evolution of the charge density (Figure 4.4), but the numerical values are quite different.

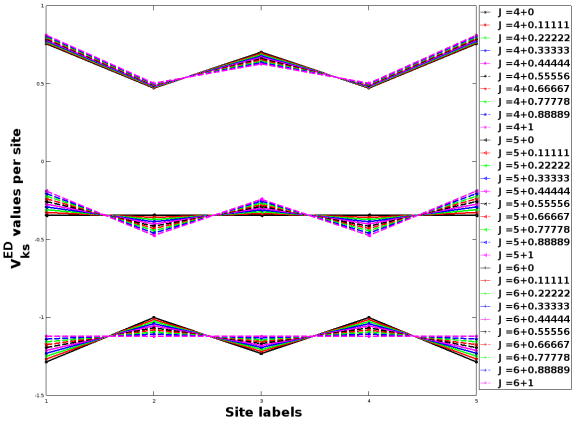


Figure 4.1: Exact KS potential as a function of particle number for particles in an infinite square well.

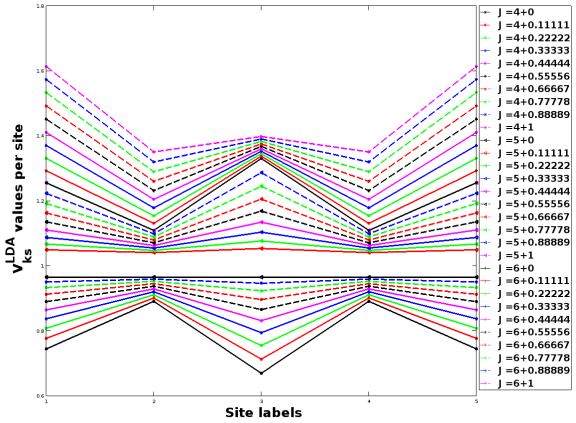


Figure 4.2: KS potential in the LDA approximation as a function of particle number for particles in an infinity square well.

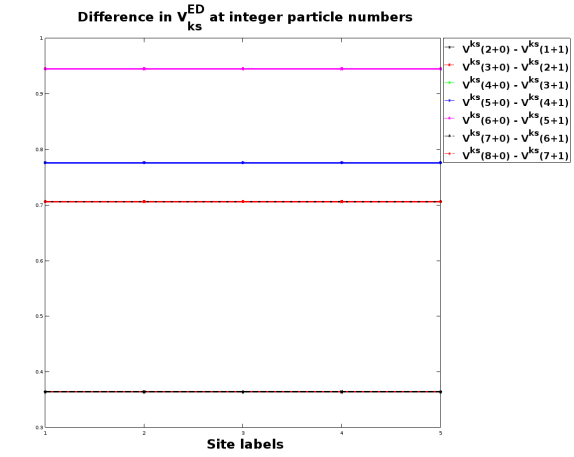


Figure 4.3: Difference in the exact KS potentials at integer particle numbers for J approaching an integer from above and below.

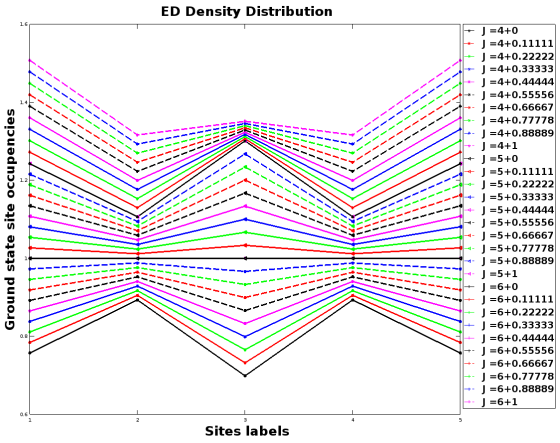


Figure 4.4: Variation of the ground state density.

4.5 Conclusion and Outlook

The discontinuity in the (functional) derivative of the exchange-correlation plus Hartree energy was confirmed for a finite Hubbard model. This is seen in the exact KS potential which changes continuously for particle numbers between integers, but for which there is a spatially independent discrete jump as the particle number passes through an integer. For comparison, the charge density is continuous and the approximate LDA-KS potential is continuous at integer particle numbers. A site derivative discontinuity in the LDA at site density $n_i = 1$ gives rise to a rapid change in the LDA-KS potential at half filling, but the LDA-KS potential is a continuous function of particle number. The discontinuity in the KS potential at integer particle numbers is at the heart of the problem of determining the fundamental gap from KS calculations [51]. As a further study we intend to explore an ensemble

definition of the excahnge-correlation energy to construct approximations to the KS potential that includes a discontinuity at integer particle numbers.

Chapter 5

Self-consistent Hartree plus Exchange Approximation

5.1 "Hartree plus exchange"potential

As seen in Section 3.3.2, the KS potential can be split into different parts. For the implementation of the Hartree plus Exchange approximation, let us consider

$$v^{KS} = v^{Hx} + v^c + v.$$

We can then, from the Hartree plus exchange energy E^{Hx}, define the potential as

$$v_i^{Hx}(n_e) = \frac{d}{d\rho_i} E^{Hx}(n_e). \tag{5.1}$$

We then remain with a proper definition of E^{Hx}. In fact, the KS ground state wave function being antisymmetric bears the correlation due to exchange of two electron positions. Since it gives the interacting density back, it further can be used to retrieve the Hartree energy between two electrons. From these observations, the definition of the Hartree plus exchange energy arises,

$$E^{Hx}(n_e) = \langle \Phi(n_e) \, | \hat{u} | \, \Phi(n_e) \rangle \, . \tag{5.2}$$

Eq. (5.2) shows that E^{Hx} is an explicit function of the KS ground state wave function; however, v^{Hx} is the response function of varying the energy with respect to the particle density. Therefore, one has to use the chain rules via a new variable that ought to link Φ and ρ. A suitable genuine variable is the KS potential. Thus,

$$\begin{aligned} v_i^{Hx}(n_e) &= \sum_j \frac{dE^{Hx}}{dv_j^{KS}}(n_e) \frac{dv_j^{KS}}{d\rho_i}(n_e) \\ &= 2 \sum_j \left\langle \frac{d\Phi}{dv_j^{KS}} \, | \hat{u} | \, \Phi \right\rangle (n_e) \frac{dv_j^{KS}}{d\rho_i}(n_e). \end{aligned}$$

On one hand, for

$$\Phi = \sum_{k=1}^{M} b_k \phi_k,$$

one finds out that:

$$\hat{H}^{KS}\Phi = E^{KS}\Phi \Longrightarrow (\hat{H}^{KS} - E^{KS})\frac{d\Phi}{dv_j^{KS}} = (\frac{dE^{KS}}{dv_j^{KS}} - \frac{d\hat{H}^{KS}}{dv_j^{KS}})\Phi \tag{5.3}$$

$$\Longrightarrow (\hat{H}^{KS} - E^{KS})\frac{d\Phi}{dv_j^{KS}} = (\frac{dE^{KS}}{dv_j^{KS}} - \hat{n}_j)\Phi. \tag{5.4}$$

By performing the braket product of Eq. (5.4) with $\langle\Phi|$ and also with $\langle\phi_k|$, one gets

$$\left\langle \Phi \middle| (\frac{dE^{KS}}{dv_j^{KS}} - \hat{n}_j)\Phi \right\rangle = 0 \tag{5.5a}$$

$$\left\langle \phi_k \middle| (\hat{H}^{KS} - E^{KS})\frac{d\Phi}{dv_j^{KS}} \right\rangle = \left\langle \phi_k \middle| (\frac{dE^{KS}}{dv_j^{KS}} - \hat{n}_j)\Phi \right\rangle. \tag{5.5b}$$

So,

$$Eq(5.5a) \Longrightarrow \frac{dE^{KS}}{dv_j^{KS}} = \langle\Phi\,|\hat{n}_j|\,\Phi\rangle \tag{5.6}$$

$$\Longrightarrow \frac{dE^{KS}}{dv_j^{KS}} = \rho_j; \tag{5.7}$$

and

$$\begin{aligned}
Eq(5.5b) &\Longrightarrow \sum_{m=1}^{M} \left\langle \phi_k \middle| (\hat{H}^{KS} - E^{KS})\frac{db_m}{dv_j^{KS}}\phi_m \right\rangle = \sum_{m=1}^{M} \left\langle \phi_k \middle| (\frac{dE^{KS}}{dv_j^{KS}} - \hat{n}_j)b_m\phi_m \right\rangle \\
&\Longrightarrow \sum_{m=1}^{M} \frac{db_m}{dv_j^{KS}} \left\langle \phi_k \middle| (\hat{H}^{KS} - E^{KS})\phi_m \right\rangle = \sum_{m=1}^{M} b_m \left\langle \phi_k \middle| (\frac{dE^{KS}}{dv_j^{KS}} - \hat{n}_j)\phi_m \right\rangle \\
&\Longrightarrow \sum_{m\neq k} \frac{db_m}{dv_j^{KS}} \left\langle \phi_k \middle| \hat{T}\phi_m \right\rangle + \frac{db_k}{dv_j^{KS}} \langle \phi_k \,|\hat{v}^{KS} - E^{KS}|\, \phi_k \rangle = b_k \langle \phi_k \,|(\rho_j - \hat{n}_j)\phi_k \rangle \\
&\Longrightarrow \sum_{m\neq k} \left\langle \phi_k \middle| \hat{T}\phi_m \right\rangle \frac{db_m}{dv_j^{KS}} + \left(\langle \phi_k \,|\hat{v}^{KS}\phi_k \rangle - E^{KS}\right) \frac{db_k}{dv_j^{KS}} = (\rho_j - \langle \phi_k \,|\hat{n}_j\phi_k \rangle)\, b_k \\
&\Longrightarrow \sum_{m=1}^{M} \left[(1-\delta_{km}) \left\langle \phi_k \middle| \hat{T}\phi_m \right\rangle + \delta_{km} \left(\langle \phi_k \,|\hat{v}^{KS}\phi_k \rangle - E^{KS}\right)\right] \frac{db_m}{dv_j^{KS}} = (\rho_j - \langle \phi_k \,|\hat{n}_j\phi_k \rangle)\, b_k.
\end{aligned} \tag{5.8}$$

Let us rewrite Eq. (5.8) using matrices. First, let b be the column vector $(b_s)_{1\leq s\leq M}^{\tau}$ of the components of Φ where τ stands for the transpose. This implies that

$$\frac{db}{dv_j^{KS}} = (\frac{db_s}{dv_j^{KS}})_{1\leq s\leq M}^{\tau}.$$

Finally for j, m and k let us denote

$$\left[(1-\delta_{km}) \left\langle \phi_k \middle| \hat{T}\phi_m \right\rangle + \delta_{mk} \left(\langle \phi_k \,|\hat{v}^{KS}\phi_k \rangle - E^{KS}\right)\right]_{km}$$

and

$$[(\rho_j - \langle \phi_k \,|\hat{n}_j\phi_k \rangle)b_k]_k^{\tau}$$

by the matrix A and the column vector B^j respectively. In other words, Eq(5.8) is equivalent to

$$A\frac{db}{dv_j^{KS}} = B^j. \tag{5.9}$$

The changes of the wave function stem from Eq. (5.9) by inverting the matrix A. This unfortunately rises the problem of invertibility. Nonetheless, one can avoid this by using singular value decomposition.

On the other hand, for

$$\rho_i = \langle \Phi \left| \hat{n}_i \right| \Phi \rangle ,$$

one gets

$$\frac{d\rho_i}{dv_j^{KS}} = 2 \left\langle \frac{d\Phi_m}{dv_j^{KS}} \left| \hat{n}_i \right| \Phi \right\rangle \tag{5.10}$$

$$= 2 \sum_{m=1}^{M} \frac{db_m}{dv_j^{KS}} \langle \phi_m \left| \hat{n}_i \right| \phi_m \rangle . \tag{5.11}$$

Therefore, on can invert the matrix $(\frac{d\rho_i}{dv_j^{KS}})_{ij}$ to obtain $(\frac{dv_j^{KS}}{d\rho_i})_{ji}$ i.e. $v^{Hx}(n_e)$. The fractional number system demands an extra work in order to obtain $v^{Hx}(N)$. All this starts from the introduction of the fractional α which depends on $\rho(N)$ as follows

$$\sum_{i=1}^{L} \rho_i(N) = n_e + \alpha. \tag{5.12}$$

Indeed, the Hartree plus exchange energy takes the form

$$E^{Hx} = Tr\{\Gamma[v^{KS}(N)]\hat{u}\}.$$

More explicitly,

$$E^{Hx}(N) = (1-\alpha)E^{Hx}(n_e) + \alpha E^{Hx}(n_e+1)$$

so that

$$\begin{aligned} v_i^{Hx}(N) &= \frac{d\alpha}{d\rho_i(N)} \left(E^{Hx}(n_e+1) - E^{Hx}(n_e) \right) + (1-\alpha) \sum_j \frac{dE^{Hx}(n_e)}{dv_j^{KS}(N)} \frac{dv_j^{KS}(N)}{d\rho_i(N)} + \alpha \sum_j \frac{dE^{Hx}(n_e+1)}{dv_j^{KS}(N)} \frac{dv_j^{KS}(N)}{d\rho_i(N)} \\ &= E^{Hx}(n_e+1) - E^{Hx}(n_e) + (1-\alpha) \sum_j \frac{dE^{Hx}(n_e)}{dv_j^{KS}(N)} \frac{dv_j^{KS}(N)}{d\rho_i(N)} + \alpha \sum_j \frac{dE^{Hx}(n_e+1)}{dv_j^{KS}(N)} \frac{dv_j^{KS}(N)}{d\rho_i(N)} \\ &= E^{Hx}(n_e+1) - E^{Hx}(n_e) + (1-\alpha) v_i^{Hx}[n_e, v^{KS}(N)] + \alpha v_i^{Hx}[n_e+1, v^{KS}(N)]. \end{aligned}$$

The term $E^{Hx}(n_e+1) - E^{Hx}(n_e)$ does not change with α. It is then a spacial independent constant that uniformly shifts $v_i^{Hx}(N)$ at integer particle numbers. That is,

$$v_i^{Hx}(n_e^+) - v_i^{Hx}(n_e^-) = E^{Hx}(n_e+1) + E^{Hx}(n_e-1) + 2E^{Hx}(n_e).$$

Readily, one may figure out the difference between $v_i^{Hx}[n_e, v^{KS}(N)]$ and $v_i^{Hx}(n_e)$ where the later is obtained from $v^{KS}(n_e)$.

5.2 Density functional theory on a lattice: Self-consistent Hartree plus Exchange Approximation

5.2.1 Abstract

Within an ensemble density functional theory formulation for a finite chain single band Hubbard Hamiltonian we define a 'Hartree plus exchange' approximation that can be solved exactly in a self-consistent framework.

In this formulation we exclude a small 'correlation' term. Comparison of the results for a short Hubbard chain with the exact values shows that the discontinuity in the Kohn-Sham potential is reproduced well and that the approximate total energy is a good approximation of the exact total energy. The results suggest that it is possible to find a good approximate solution for a Hubbard chain of any length and open a way for solving interesting models such as Hubbard defect chains in a numerically simple and reliable way.

5.2.2 Introduction

In the mid 1960's Kohn with Hohenberg [1] and Sham [2] established the formal basis of Density Functional theory (DFT), a well known powerful formulation nowadays widely used by chemists and material scientists. DFT is formally exact, but the exact form of all the density functionals in the formalism, including the exchange-correlation energy, is not known. In practical applications the exchange-correlation term is approximated and unfortunately there is no systematic way to develop approximations to the exact density functionals. This has led to a confusing multitude of approximations in the literature. Approximations that have been used with success include 1) the venerable Local Density Approximation (LDA) [2, 19, 20] which is based on the properties of the homogeneous electron gas, 2) Generalized Gradient Approximations (GGA) [22, 23] where the exchange-correlation functional expression includes the gradient of the density, 3) Hybrid functionals [24, 25, 26] which include a contribution from exact exchange. Many other approximations have been proposed for many-electron systems whose spatial coordinates belong to a continuum. A systematic examination of the properties of approximations are hampered by the almost impossible task of finding exact solutions for models of real systems. Lattice DFT [27, 28] is one of the interesting ways to investigate density functionals. Here the finite chain single band Hubbard Hamiltonian has been used since it is possible to determine the exact interacting density and eigenenergies for a range of models. For example, the exact Kohn-Sham (KS) potential for this model can be studied as a function of electron number, which allows an investigation of a spatially independent discontinuity of the functional derivative of the exchange-correlation potential at integer particle numbers.

In Section 2, we summarise some important background of Lattice-DFT functionals combined with an ensemble DFT formalism necessary to fully explore the properties of density functionals. In Section 3 we introduce the approaches we used to probe the Hartree plus exchange approximation and the consequent KS potential as functions of the number of electrons in the lattice. We then present results followed by their analysis in Section 4 which leads us to the conclusion in Section 5.

5.2.3 Background

The simplest Hubbard Hamiltonian [29, 30] for a finite chain single band of length l that contains n_e electrons can be written as

$$\hat{H} = \hat{T} + \hat{u} + \hat{v}. \tag{5.13}$$

In Eq.(5.13),

$$\hat{T} = -t \sum_{\substack{1 \le i,j \le l \\ j = i \pm 1}} \sum_{\sigma = \uparrow, \downarrow} \hat{C}^{\dagger}_{j\sigma} \hat{C}_{i\sigma},$$

$$\hat{u} = u_0 \sum_{1 \leq i \leq l} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

and

$$\hat{v} = \sum_{1 \leq i \leq l} \sum_{\sigma=\uparrow,\downarrow} v_i \hat{n}_{i\sigma}$$

are the kinetic, the spin-correlation and the external potential operators respectively. At zero temperature, the ground state wave function ψ^0, solution of the Schrödinger equation

$$\hat{H}\psi^i = E_i \psi^i,$$

helps to determine the ground state site-density

$$\rho_i^0 = \left\langle \psi^0 \left| \sum_\sigma \hat{n}_{i\sigma} \right| \psi^0 \right\rangle$$

and the ground state energy

$$E_0 = \left\langle \psi^0 \left| \hat{H} \right| \psi^0 \right\rangle.$$

If the ground state energy of a system that exchanges particles with a particle reservoir satisfies the convexity condition [49, 50, 51],

$$E_0(n_e) - E_0(n_e - 1) \leq E_0(n_e + 1) - E_0(n_e),$$

it leads to the simple two state ensemble

$$\Gamma_\alpha[v] = (1-\alpha) \left| \psi^0[n_e, v] \right\rangle \left\langle \psi^0[n_e, v] \right| + \alpha \left| \psi^0[n_e + 1, v] \right\rangle \left\langle \psi^0[n_e + 1, v] \right|$$

where α $(1-\alpha)$ is the probability of finding the system in the state $\psi^0[n_e + 1]$ $(\psi^0[n_e])$. For a system in a state with

$$N = n_e + \alpha$$

electrons, where n_e is an integer, the expectation value of any observable $\hat{O}$ is

$$\langle O \rangle = Tr \left\{ \Gamma_\alpha[v] \hat{O} \right\},$$

where Tr is the trace of the product of the two operators. In the KS framework [2], we map the interacting system onto a fictitious noninteracting system with Hamiltonian

$$\hat{H}_{KS} = \hat{T} + \hat{v}^{KS}, \tag{5.14}$$

with potential v^{KS}, unique up to a constant, which reproduces the exact interacting electronic (site-) density of the interacting ground state. The ground state energy can be partitioned as

$$\begin{aligned} E_0(N) &= Tr\{\Gamma_\alpha H\} \\ &= T^{KS} + E^{Hx} + E^c + Tr\left\{\Gamma_\alpha[v^{KS}]\hat{v}\right\}, \end{aligned} \tag{5.15}$$

where the last expression follows since $\Gamma_\alpha[v^{KS}]$ and $\Gamma_\alpha[v]$ yield the same ground state density by construction. For historical reasons, we call E^{Hx} the Hartree plus exchange energy term and E^c the correlation energy, while T^{KS} is the kinetic energy of the noninteracting Kohn-Sham system. In Eq. (5.15),

$$T^{KS} = Tr\left\{\Gamma_\alpha\left[v^{KS}\right]\hat{T}\right\}, \tag{5.16}$$

$$E^{Hx} = Tr\left\{\Gamma_\alpha\left[v^{KS}\right]\hat{u}\right\}, \tag{5.17}$$

$$E^c = Tr\left\{\Gamma_\alpha\left[v\right]\left(\hat{T}+\hat{u}\right)\right\} - Tr\left\{\Gamma_\alpha\left[v^{KS}\right]\left(\hat{T}+\hat{u}\right)\right\} \tag{5.18}$$

and the Kohn-Sham potential is

$$\hat{v}^{KS} = \hat{v}^{Hx} + \hat{v}^{c} + \hat{v},$$

where v^{Hx} is the functional derivative of E^{Hx} and v^c this of E^c. The correlation energy E^c is expected to make a small contribution to the total energy as confirmed below and in the Hartree plus exchange approximation we set this term to zero with the resultant approximate Kohn Sham potential

$$\hat{\tilde{v}}^{KS} = \hat{\tilde{v}}^{Hx} + \hat{v}. \tag{5.19}$$

It is useful to define $\tilde{E}^{Hxv} = \tilde{E}^{Hx} + Tr\left\{\Gamma_\alpha[\tilde{v}^{KS}]\hat{v}\right\}$ so that $E_0 = \tilde{T}^{KS} + \tilde{E}^{Hxv} + \tilde{E}^c$ i.e. $\tilde{E}^c = E_0 - [\tilde{T}^{KS} + \tilde{E}^{Hxv}]$. This definition of $\tilde{E}^c$ is exact for the exact DFT equations and is an approximation of the correlation energy in the Hartree plus exchange approximation.

5.2.4 Method

For any allowed number of electrons for a finite lattice, fractional or integer, we start by solving the exact interacting Hubbard Hamiltonian numerically and then solve the KS equation self-consistently to obtain the exact KS potential v^{KS}. This gives us the exact results to which approximations can be compared. Using Eq. (5.19) it is possible to solve the Hartree plus exchange approximation within the Kohn-Sham formulation. We first perform an exact diagonalization of an initial KS Hamiltonian with an approximate potential v_0^{KS}. Using the perturbation theory, we compute $\frac{\partial\phi^0}{\partial v^{KS}}$ from which we determine $\frac{\partial\rho^0}{\partial v^{KS}}$ and $\tilde{v}_0^{Hx}$. Finally we obtain a new KS potential v_1^{KS} using Eq. (5.19). This process is repeated until a self-consistent approximate KS potential $\tilde{v}^{KS}$ is obtained. From now on, let us consider a lattice of 4 sites with a flat external potential $v = (1, 1, 1, 1)^T$. We choose this potential to highlight the site dependence of the exchange-correlation potential. For this model we are interested in the KS potential for electron number N in the range $1 \leq N \leq 8$. Let us set, in arbitrary units, the hopping term t to be 1 while the on-site coulomb potential u is set to 2.
All the results discussed in this paper were calculated with codes written in Octave [75].

5.2.5 Results and analysis

The exact KS potential shows a site independent discontinuity at integer particle numbers (Figure 5.1) if we compare the potential as we approach an integer particle number from below or above. The approximate KS potential (Figure 5.2) reproduces the shape and the discontinuity observed for the

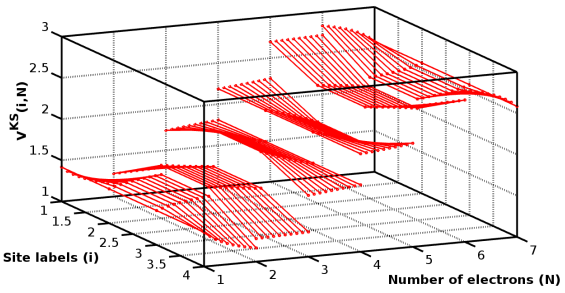


Figure 5.1: Exact KS potential v^{KS} as a function of particle number for a finite chain.

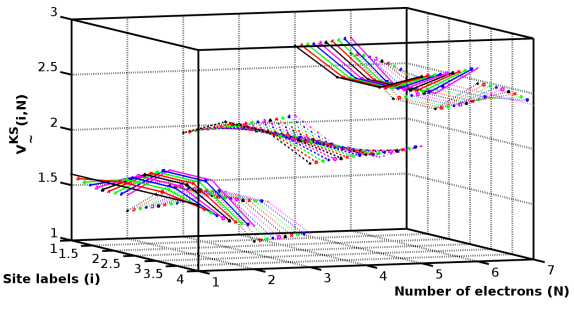


Figure 5.2: Approximate KS potential $\tilde{v}^{KS}$ as a function of particle number for a finite chain.

exact potential. In Figures 5.3 and 5.4, we notice a shift of the approximate potential with respect to the exact one. The Hartree plus exchange potential has the form

$$v_i^{Hx}(N) = (1-\alpha)v_i^{Hx}[n_e, v^{KS}(N)] + \alpha v_i^{Hx}[n_e+1, v^{KS}(N)] + E^{Hx}(n_e+1) - E^{Hx}(n_e),$$

where n_e is an integer and $n_e \leq N \leq n_e+1$. The first two terms describe the shape of the potential and the last two terms are particle number dependent but site independent constants. These constants change when N passes through an integer and give rise to a site independent discontinuity in the potential at integer particle numbers.

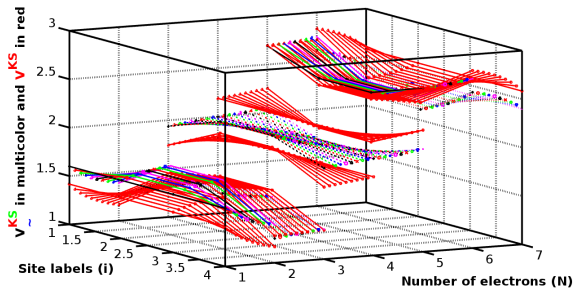


Figure 5.3: 3D plot of the exact and the approximate KS potentials.

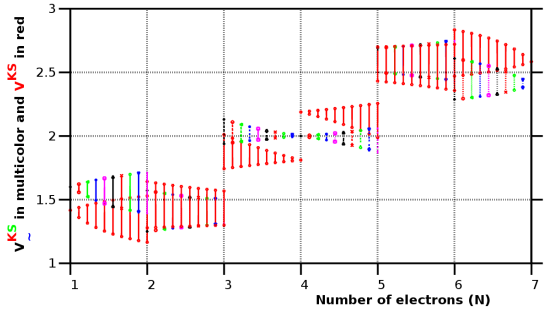


Figure 5.4: 2D plot of the exact and the approximate KS potentials.

The maximum percentage error between the exact and approximate kinetic energies is less than 0.26% while for the Hartree plus exchange energy it is 1.09%. This is interesting since it reveals the similarity between ϕ^0 and $\tilde{\phi}^0$, the exact and approximate KS ground state wave functions. Figure 5.5 shows the maximum and minimum, over all the sites, percentage error in the ground state density. The highest percentage error is 3.12%. The difference between the curves in Figure 5.6 gives an indication of the size of E^c. The correlation energy decreases at high filling while it reaches its maximum around a filling of 3. The overall behaviour shows that

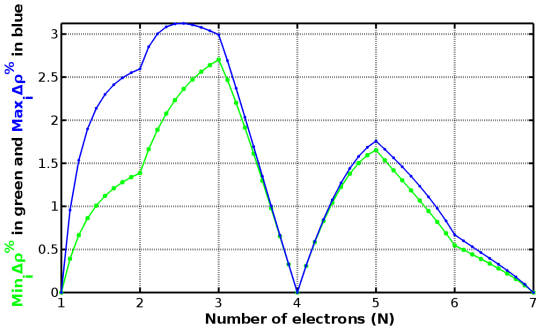


Figure 5.5: Maximum and minimum density percentage error.

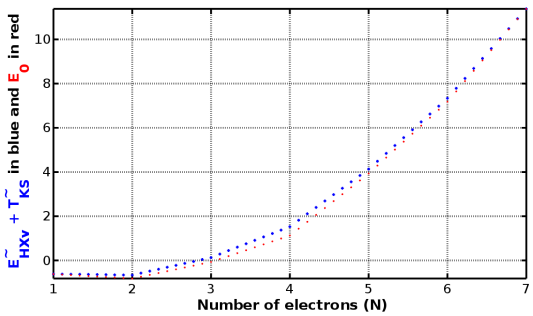


Figure 5.6: Correlation energy.

the correlation energy makes a relatively small contribution to the total energy of the system.

5.2.6 Conclusion and Outlook

We have performed a self-consistent calculation of the Hartree plus exchange approximation, a new DFT approximation applied to the Hubbard model. We found that the approximate KS potential has

a similar shape when compared to exact results. The correlation energy, estimated by the difference between the exact and approximate total energies (Figure 5.6), makes a small contribution to the total energy. From the similarity between the exact and approximate electronic densities, we confirm that the approximate KS potential has a shape which closely follows that exact potential. Future work includes an attempt to include correlations using a Jastrow factor to map the KS wave function onto the interacting wave function.

Chapter 6

Exact method for finite one dimensional lattice density functional theory

In Chapter 5 we illustrated numerically that the Hartree+Exchange approximation works well for the Hubbard model. In this approximation the DFT correlation energy is ignored. In this chapter a new approach to solve the Kohn-Sham Density Functional Theory (KS-DFT) [1, 2] problem is introduced. We map the coefficients of an expansion of the KS ground state wave function in terms of a set of basis functions onto the corresponding coefficients of the expansion for the interacting system. We develop expressions for the correlation energy and potential and a fully self-consistent algorithm for solving the Kohn-Sham formulation exactly.

6.1 Introduction

The theoretical investigation of the physics of a system made of atoms or molecules in general and electrons in particular, is a challenge. Researchers who wish to investigate ground state properties, including magnetic properties [76], metal-insulator transitions [62, 32], electronic structures, lattice parameters and elastic constants can use density functional theory which formally reduces the problem to a study of the ground state density distribution [77, 78, 79, 80]. This challenge stems from the complexity of electron correlations [63] due to the dynamic Coulomb interactions between all pairs of particles as well as quantum-mechanical interactions which are related to the anti-symmetry of the wave functions for Fermions. The latter gives rise to the Pauli exclusion principle in an independent particle description. The Pauli exclusion principle contributes to the exchange interaction [9, 25] by preventing two electrons with the same spin from occupying the same position. In the case of the Hubbard model it means that equal spin particles cannot occupy the same atomic site.

To circumvent the complexity of atomic systems, model systems like tight binding models [81, 80] are often used. This simplifies the original system to system whose electrons are tightly bounded to the nuclei in a manner that the valence electron wave functions can only overlap with the closest neighbouring atomic orbits; all the electrons are highly localized around the nuclei. Among those models, the Hubbard model [57, 58, 59, 60, 76] is one of the simplest.

Exact solutions, even for simple models, are few. An exception is the solution of the one dimensional single band periodic Hubbard model with nearest neighbour interactions only [37, 38]. The approach known as Bethe ansatz [39, 40, 41] allows us to work out the exact ground state wave function, energy and the chemical potential. Another approach with promise is the Kohn-Sham (KS) Density Functional method KSDFT [2]. In the KS framework, one constructs a model for fictitious noninteracting particle with the constraint that the ground state density of the latter system is equal to the ground state density of the interacting system. Though the ground state density is reproduced by the KS system, the method does not yield the interacting wave function and the total energy directly. The KS wave function partly captures the exchange and the coulomb correlations and the remainder of the correlation is called the correlation energy (E_c) [63]. Nonetheless, combined with approximations for the exchange-correlation energy [2, 51, 22, 23, 24, 26], excellent approximate total energies can be obtained. Contrary to the Bethe ansatz, KSDFT is general, it is not limited to an infinite uniform system. Approximate KSDFT is widely used nowadays: It is the standard approach to study structural and ground state properties of solids and molecules.
In Section 6.2 properties of the eigenfunction ground state energy of the one dimensional Hubbard Hamiltonian on a finite lattice are reviewed. A Jastrow factor operator is formally introduced in Section 6.2.2. Its existence is formally established and its application in calculating the correlation energy and potential follow from Sections 6.3 to 6.5. The results are analysed. In Section 6.6, we establish a self-consistent KS calculation of the Jastrow factors as well as the KS and the interacting ground state properties. Finally, Section 6.7 comes to summarize the work done.

6.2 Exact method: Jastrow factor operator

6.2.1 Hubbard Hamiltonian and its ground state wave function

The one dimensional Hubbard Hamiltonian

Let us consider a L site one dimensional lattice occupied by n_e electrons. The physical behaviour of the electrons can be probed by the one dimensional Hubbard Hamiltonian

$$\hat{H}^\lambda = \hat{T} + \lambda\hat{u} + \hat{v}^\lambda, \tag{6.1}$$

where

$$\begin{aligned}
\hat{T} &= \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{L}\sum_{1\le j=i\pm1\le L} t_{ij}\hat{C}^\dagger_{j\sigma}\hat{C}_{i\sigma} \\
&= \sum_{<i,j>,\sigma}^{L} t_{ij}\hat{C}^\dagger_{j\sigma}\hat{C}_{i\sigma}, \\
\hat{u} &= u_0\sum_{i=1}^{L}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}, \\
\hat{v}^\lambda &= \sum_{\sigma=\uparrow,\downarrow}\sum_{i=1}^{L} v_i^\lambda\hat{n}_{i\sigma}.
\end{aligned}$$

The parameters t_{ij}, u_0 and v_i^λ stand for the hopping term that quantifies the energy change associated when an electron at site i jumps to site j, the coulomb interaction term and the on-site external

potential respectively. The site potential v_i^λ is constructed to keep the ground state charge density independent of λ, the adiabatic connection coefficient. When $\lambda = 1$, we recover the fully interacting system and when $\lambda = 0$ we have the independent particle Kohn-Sham system.

The operator $\hat{C}_{i\sigma}^\dagger$ ($\hat{C}_{i\sigma}$) is the creation (annihilation) operator and

$$\hat{n}_{i\sigma} = \hat{C}_{i\sigma}^\dagger \hat{C}_{i\sigma}$$

is the on-site spin σ number operator. We only consider nearest neighbour hopping and set

$$t_{ij} = -t\delta_{i,j\pm1},$$

with t a positive real number, $1 \leq i, j \leq L$.

A spin σ electron at site i is represented by the wave function $\hat{C}_{i\sigma}^\dagger|\rangle$ and a Slater determinant wave function $|\phi_m\rangle$ of n_e electrons is given by operating with n_e creation operators on the vacuum state $|\rangle$,

$$|\phi_m\rangle = \hat{C}_{m_1\uparrow}^\dagger \hat{C}_{m_2\uparrow}^\dagger \cdots \hat{C}_{m_{N_\uparrow}\uparrow}^\dagger \hat{C}_{m_{N_\uparrow+1}\downarrow}^\dagger \hat{C}_{m_{N_\uparrow+2}\downarrow}^\dagger \cdots \hat{C}_{m_{N_\uparrow+N_\downarrow}\downarrow}^\dagger |\rangle, \tag{6.2}$$

where the number of up-spin, $N_\uparrow$, and down-spin, $N_\downarrow$, particles sum to n_e. The form we have adopted for the wave $|\phi_m\rangle$ in Eq. (6.2) is one of the n_e factorial possible arrangements of the elements $\hat{C}_{m_1\uparrow}^\dagger$, $\hat{C}_{m_2\uparrow}^\dagger$, $\cdots$, $\hat{C}_{m_{N_\uparrow}\uparrow}^\dagger$, $\hat{C}_{m_{N_\uparrow+1}\downarrow}^\dagger$, $\hat{C}_{m_{N_\uparrow+2}\downarrow}^\dagger$, $\cdots$, $\hat{C}_{m_{N_\uparrow+N_\downarrow-1}\downarrow}^\dagger$ and $\hat{C}_{m_{N_\uparrow+N_\downarrow}\downarrow}^\dagger$. The set

$$\Xi = \left\{ |\phi_m\rangle \,\middle|\, 1 \leq m \leq \sum_{N_\uparrow=\max(0,n_e-L)}^{\min(n_e,L)} \binom{N_\uparrow}{L}\binom{N_\downarrow}{L} \right\}$$

and each of its subsets

$$\Xi_w = \left\{ |\phi_m\rangle \,\middle|\, 1 \leq m \leq \binom{N_\uparrow^w}{L}\binom{N_\downarrow^w}{L} \text{ and } N_\uparrow^w \text{ is fixed} \right\}$$

form an orthonormal (sub-) basis for the n_e-electron (sub-) Hilbert space. A solution of the Schrödinger equation $\hat{H}^\lambda \varsigma^\lambda = E^\lambda \varsigma^\lambda$ provides the wave functions ς^λ and eigenenergies E^λ. An exact diagonalization of the Hubbard Hamiltonian matrix [74] that arises from the choice of the basis set Ξ is one of the many ways the solution can be done. The cardinal of Ξ grows very fast with the number of sites or electrons. However, since the Hubbard Hamiltonian commutes with the spin number operator

$$\hat{S} = \sum_{i=1}^{n_e} \frac{\hat{n}_{i\uparrow} - \hat{n}_{i\downarrow}}{2}$$

and n_e is fixed for a given system, the Hamiltonian matrix is block diagonalizable. Therefore we only have to consider basis functions with the same total spin when looking for eigenfunctions of the Hamiltonian which correspond to the sub-bases Ξ_w. The ground state of the interacting system with a given total spin is of the form

$$|\Psi\rangle = \sum_{\Xi_0} f_m |\phi_m\rangle \tag{6.3}$$

and that of the noninteracting system is

$$|\Phi\rangle = \sum_{\Xi_0} g_m |\phi_m\rangle , \tag{6.4}$$

where each of the $|\phi_m\rangle$ has the same total spin.

It turns out that the choice of the sign of t has no effect on the eigenspectrum. The explicit proof of this statement given below is based on the hint given by Lieb and Wu in [37] for a periodic system. We show that it is general and that it applies to arbitrary length models.

Consider the unitary transformation

$$\mathcal{O} = e^{i\pi \sum_{j,\sigma_j} \hat{n}_{j\sigma}},$$

For any $|\phi_m\rangle \in \Xi$ and all $1 \leq k \leq L$,

$$\begin{aligned}
\mathcal{O}^\dagger \hat{t}_{kk\pm1,\sigma} \mathcal{O} |\phi_m\rangle &= e^{-i\pi \sum_{j,\sigma_j} \hat{n}_{j\sigma_j}} \hat{t}_{kk\pm1,\sigma} e^{i\pi \sum_{j,\sigma_j} \hat{n}_{j\sigma_j}} |\phi_m\rangle \\
&= e^{i\pi(n_{k\sigma} - n_{k\pm1\sigma})} \hat{t}_{kk\pm1,\sigma} |\phi_m\rangle \\
&= \delta_{(n_{k\sigma}-1)} \delta_{n_{k\pm1}} e^{i\pi} \hat{t}_{kk\pm1,\sigma} |\phi_m\rangle \\
&= -\hat{t}_{kk\pm1,\sigma} |\phi_m\rangle . \qquad (6.5)
\end{aligned}$$

This leads to

$$\mathcal{O}^\dagger \hat{T} \mathcal{O} = -\hat{T}$$

and, since $\mathcal{O}$ is unitary and commutes with $\hat{u}$ and $\hat{v}^\lambda$,

$$\mathcal{O}^\dagger \hat{H}^\lambda \mathcal{O} = -\hat{T} + \lambda \hat{u} + \hat{v}^\lambda.$$

For an arbitrary eigenfunction $\left|\varsigma^\lambda\right\rangle$ of $\hat{H}^\lambda$,

$$\mathcal{O}^\dagger \hat{H}^\lambda \mathcal{O} \left|\varsigma^\lambda\right\rangle = E^\lambda \left|\varsigma^\lambda\right\rangle ,$$

as shown below. The eigensolutions

$$(\hat{H}^\lambda - E^\lambda) \left|\varsigma^\lambda\right\rangle = 0$$

can be written as

$$(\hat{H}^\lambda - \mathcal{O} E^\lambda \mathcal{O}^\dagger) \left|\varsigma^\lambda\right\rangle = 0$$

since

$$\mathcal{O}^\dagger \mathcal{O} = \hat{\mathbf{1}}. \qquad (6.6)$$

Using Eq. (6.6) repeatedly we find that

$$\begin{aligned}
\mathcal{O}(\mathcal{O}^\dagger \hat{H}^\lambda \mathcal{O} - E^\lambda)\mathcal{O}^\dagger \left|\varsigma^\lambda\right\rangle &= 0 \\
(\mathcal{O}^\dagger \hat{H}^\lambda \mathcal{O} - E^\lambda)\mathcal{O}^\dagger \left|\varsigma^\lambda\right\rangle &= 0
\end{aligned}$$

and finally

$$\left(-\hat{T} + \lambda \hat{u} + \hat{v}^\lambda\right) \mathcal{O}^\dagger \left|\varsigma^\lambda\right\rangle) = E^\lambda \mathcal{O}^\dagger \left|\varsigma^\lambda\right\rangle . \qquad (6.7)$$

This shows that if we replace t by $-t$, the eigenfunction $\left|\varsigma^\lambda\right\rangle$ is mapped onto $\mathcal{O}^\dagger \left|\varsigma^\lambda\right\rangle$, but the eigenenergy E^λ remains unchanged. The eigenspectrum is therefore independent of the sign of t while the wave functions can differ when the sign of t is changed. However, if the wave functions are solved for a given t, the corresponding wave functions for $-t$ can be determined operating with $\mathcal{O}$ on the wave function.

Note that the transformation $\mathcal{O}^\dagger \hat{H}^\lambda \mathcal{O} = -\hat{T} + \lambda \hat{u} + \hat{v}^\lambda$ is not general. The interaction operator $\hat{u}$ commutes with $\mathcal{O}$ only if we retain the onsite interaction terms only. Similarly, $\mathcal{O}^\dagger \hat{T} \mathcal{O} = -\hat{T}$ if we retain nearest neighbour hopping only.

Positive ground state wave function components

In this section we show that for positive t the sign of the coefficients (g or f in Eqs. (6.3) and (6.4)) for the ground state are the same for a Hubbard model with nearest neighbour hopping and on-site

interaction. Here we give an explicit proof of the statement by Lieb and Wu given in reference [71], but which does not appear in the literature. We show that the observation is valid for a finite chain with nearest neighbour hopping and on-site interactions for the interacting as well as noninteracting systems.

Let x_i^m ($1 \leq x_i^m \leq L$ and $1 \leq i \leq n_e$) label the sites where up-spin and down-spin particles are found for each basis wave function $|\phi_m\rangle$. The up-spin particles are found at $x_1^m, x_2^m, \cdots, x_{N_\uparrow}^m$ and the down-spin particles at $x_{N_\uparrow+1}^m, x_{N_\uparrow+2}^m, \cdots, x_{n_e}^m$. The coefficients f_m and g_m of the wave functions, expressed in Eqs. (6.3) and (6.4), can be thought of as functions f and g that map the n_e-tuples

$$x^m = (x_1^m, x_2^m, \cdots, x_{n_e}^m) \tag{6.8}$$

into the real numbers

$$f(x^m) = f_m$$

and

$$g(x^m) = g_m.$$

Let $h^\lambda(x^m)$ be the generic expansion coefficient of basis function $|\phi_m\rangle \equiv |x_1^m \cdots x_{n_e}^m\rangle$ in the eigenfunctions of H^λ,

$$\left|\varsigma^\lambda\right\rangle = \sum h^\lambda(x^m)|x_1^m \cdots x_{n_e}^m\rangle.$$

We recall that we reserved f_m and g_m for the interacting and noninteracting systems, respectively. Acting with $\hat{H}^\lambda$ on $\left|\varsigma^\lambda\right\rangle$ leads to

$$\begin{aligned}
\hat{H}^\lambda \left|\varsigma^\lambda\right\rangle &= -t \sum_m h^\lambda(x^m) \sum_{i=1}^{n_e} \sum_{s=\pm 1} |x_1^m \cdots x_i^m + s \cdots x_{n_e}^m\rangle + \lambda u_0 \sum_m \sum_{i<j}^{n_e} \delta_{x_i^m x_j^m} h^\lambda(x^m)|x_1^m \cdots x_{n_e}^m\rangle \\
&+ \sum_m \sum_{i=1}^{L} \sum_{j=1}^{n_e} v_i^\lambda \delta_{i x_j^m} h^\lambda(x^m)|x_1^m \cdots x_{n_e}^m\rangle \\
&= E^\lambda \left|\varsigma^\lambda\right\rangle.
\end{aligned}$$

Upon taking the projection with respect to $\langle x_1, \cdots x_{n_e}|$, this leads to

$$\begin{aligned}
&- t \sum_{i=1}^{n_e} \sum_{s=\pm 1} h^\lambda(x_1, \cdots, x_i + s, \cdots, x_{n_e}) + \lambda u_0 h^\lambda(x) \sum_{i<j}^{n_e} \delta_{x_i x_j} + h^\lambda(x) \sum_{i=1}^{L} \sum_{j=1}^{n_e} v_i^\lambda \delta_{i x_j} \\
&= E^\lambda h^\lambda(x_1, \cdots, x_{n_e}).
\end{aligned} \tag{6.9}$$

The first term follows from the fact that the kinetic energy part of the Hamiltonian maps basis functions to basis wave functions that differ by 'one hop' only. In the second term we note that the expectation value of the interaction term is diagonal in the basis wave functions. For a given x^m any of the first $N_\uparrow$ x_i^m's can be equal to any of the last $N_\downarrow$ entries with corresponding expectation value of the interaction energy equal to $\lambda n u_0$, where n is the number of sites in x^m with both up-spin and down-spin occupations.

In addition for Fermions only distinct single particle states can appear in the Slater determinants and therefore

$$h^\lambda(x_1, \cdots, x_{n_e}) = 0$$

if any two values in either subset (spin-up or spin-down) are equal. For a finite chain we also demand that

$$h^\lambda(x_1 - 1, \cdots, x_{n_e}) = 0$$

if $x_1 - 1 < 1$;

$$h^\lambda(x_1, \cdots, x_{n_e} + 1) = 0$$

if $x_{n_e} + 1 > L$;

$$h^\lambda(x_1, \cdots, x_{N_\uparrow} + 1, \cdots, x_{n_e}) = 0$$

if $x_{N_\uparrow} + 1 > L$ and

$$h^\lambda(x_1, \cdots, x_{N_\uparrow+1} - 1, \cdots, x_{n_e}) = 0$$

if $x_{N_\uparrow+1} - 1 < 1$. Since $\left|\varsigma^\lambda\right\rangle$is a normalized ground state wave function,

$$\begin{aligned}\langle\varsigma^\lambda|\hat{H}^\lambda|\varsigma^\lambda\rangle &= -t\sum_m h^\lambda(x^m)\sum_{i=1}^{n_e}\sum_{s=\pm1} h^\lambda(x_1^m, \cdots, x_i^m + s, \cdots, x_{n_e}^m) \\ &+ \lambda u_0 \sum_m \sum_{i<j}^{n_e} \delta_{x_i x_j}[h^\lambda(x^m)]^2 + \sum_m \sum_{i=1}^{L}\sum_{j=1}^{n_e} v_i^\lambda \delta_{i x_j}[h^\lambda(x^m)]^2 \\ &= E^\lambda. \end{aligned} \tag{6.10}$$

Consider now the wave function $\left|\varsigma'^\lambda\right\rangle$ defined by

$$h'^\lambda(x) = |h^\lambda(x)|$$

and take the expectation value of $\hat{H}^\lambda$,

$$\begin{aligned}\langle\varsigma'^\lambda|\hat{H}^\lambda|\varsigma'^\lambda\rangle &= -t\sum_m |h^\lambda(x^m)|\sum_{i=1}^{n_e}\sum_{s=\pm1} |h^\lambda(x_1^m, \cdots, x_i^m + s, \cdots, x_{n_e}^m)| \\ &+ \lambda u_0 \sum_m \sum_{i<j}^{n_e} \delta_{x_i x_j}|h^\lambda(x^m)|^2 + \sum_m \sum_{i=1}^{L}\sum_{j=1}^{n_e} v_i^\lambda \delta_{i x_j}|h^\lambda(x^m)|^2. \end{aligned} \tag{6.11}$$

Now,

$$\begin{aligned}&\left|h^\lambda(x^m)\right| \sum_{s=\pm1} \left|h^\lambda(x_1^m, \cdots, x_i^m + s, \cdots, x_{n_e}^m)\right| \\ &\geq \left|h^\lambda(x^m) \sum_{s=\pm1} h^\lambda(x_1^m, \cdots, x_i^m + s, \cdots, x_{n_e}^m)\right| \\ &\geq h^\lambda(x^m) \sum_{s=\pm1} h^\lambda(x_1^m, \cdots, x_i^m + s, \cdots, x_{n_e}^m), \end{aligned} \tag{6.12}$$

where the last $\geq$ sign becomes $>$ if the term is negative. Since we only consider $t > 0$, it follows from Eqs. (6.10), (6.11) and (6.12) that

$$\langle\varsigma'^\lambda \hat{H}^\lambda \varsigma'^\lambda\rangle \leq \langle\varsigma^\lambda \hat{H}^\lambda \varsigma^\lambda\rangle.$$

Since ς^λ is already a ground state, it follows that

$$\langle\varsigma'^\lambda \hat{H}^\lambda \varsigma'^\lambda\rangle \geq \langle\varsigma^\lambda \hat{H}^\lambda \varsigma^\lambda\rangle.$$

The last two equations imply that ς'^λ is also a ground state. We now know that h'^λ defines a ground state and that

$$h'^\lambda(x^m) \geq 0$$

for all m. However, if there exists a m_0 such that

$$h'^\lambda(x^{m_0}) = 0,$$

we know from Eq. (6.9) that

$$-t\sum_{i=1}^{n_e}\sum_{s=\pm 1}|h'^{\lambda}(x_1^{m_0},\cdots,x_i^{m_0}+s,\cdots,x_{n_e}^{m_0})|=0.$$

This in turn tells us that all the $h'^{\lambda}(x^m)$ where x^m differs from x^{m_0} by one hop of a particle, are zero. This can be propagated through the chain and implies that all the

$$h'^{\lambda}(x^m)=0.$$

As a consequence, for a ground state defined by h we have

$$h(x)>0.$$

Now assume that the ground state is degenerated with ground states defined by coefficients h and h^1 . Then if we define expansion coefficients

$$h'=h+\nu h^1$$

will also define a ground state (not necessarily normalized). The parameter ν is arbitrary and we can choose it with at least one

$$h'(x)=0$$

that is

$$\nu=\frac{-h(x)}{h^1(x)}.$$

However, from the discussion above, this implies that

$$h'(x)=0$$

for all x which contradicts that h' defines a ground state. The conclusion is that the ground states are non-degenerate and all expansion coefficients have the same sign. The reasoning above depends on the properties of the kinetic energy operator. It is valid for any λ so applies to the interacting as well as noninteracting systems.

Note that these observations are based on the form of Eq. (6.10), valid for nearest neighbour hopping and on-site interactions for the interacting systems. For more general forms of the Hubbard Hamiltonian it may not be correct.

6.2.2 Jastrow factor operator

The Jastrow factor

In KS-DFT, the existence of the KS potential and ground state wave function that gives the interacting system ground state density is well established [1, 2, 17]. The only restriction on the KS wave function is that it gives the correct interacting system density. It can, however, differ considerably from the interacting ground state wave function.

Recall that we define the DFT Hartree plus exchange energy as

$$E^{Hx}=\langle\Phi\,|\hat{u}|\,\Phi\rangle \tag{6.13}$$

and the correlation energy as

$$E^{c}=\left\langle\Psi\left|\hat{T}+\hat{u}\right|\Psi\right\rangle-\left\langle\Phi\left|\hat{T}+\hat{u}\right|\Phi\right\rangle. \tag{6.14}$$

We showed in Chapter 5 that the Hartree plus exchange model in which we set E^c to zero leads to reasonable results, suggesting that the correlation contribution is small, as we assumed. In the Hartree plus exchange approximation, all the functionals of relevance, Eqs. (5.15) to (5.18) are expressed explicitly in terms of the KS ground state wave function. This gives us implicit functionals [82] of the density and ables us to determine the functional derivatives using perturbation theory. Including the correlation energy functional is problematic since the formal decomposition gives us an expression which includes the many-body interacting ground state wave function $|\Psi\rangle$. Finding an accurate approximation for E^c has proven to be very difficult.

If we can find a reasonable approximation of the interacting system ground state wave function we can approximate the correlation energy from the defining equation, Eq. (6.14). In this chapter we borrow ideas from Qantum Monte Carlo methods [83, 84] and write

$$|\Psi\rangle = \hat{J}\,|\Phi\rangle\,, \tag{6.15}$$

where we hope that the 'Jastrow' factor, $\hat{J}$, will take care of correlations not captured by the KS ground state wave function.

In contrast to other attempts to map a noninteracting wave function onto an interacting wave function, we examine the expansion of the eigenfunctions in terms of basis functions:

$$|\Psi\rangle = \sum_{\Xi_0} f_m\,|\phi_m\rangle$$

and

$$|\Phi\rangle = \sum_{\Xi_0} g_m\,|\phi_m\rangle\,.$$

Here we expand the interacting, $|\Psi\rangle$, and noninteracting, $|\Phi\rangle$, ground state eigenfunctions in terms of the same many-particle basis functions $|\phi_m\rangle$. Apart from pathological cases where the expansion coefficients g_m are zero and the corresponding coefficients f_m are non-zero, it is possible to define a 'Jastrow factor ' γ_m which gives the exact relationship between f_m and g_m,

$$f(x^m) = e^{-\gamma_m} g(x^m). \tag{6.16}$$

All parameters in the Hubbard Hamiltonian are real and we choose to work in real space, and therefore f_m, g_m and γ_m are all real.

Let us consider an n_e-tuple $(x_1^m \cdots x_{n_e}^m)$ which defines our chosen set of basis functions $|\phi_m\rangle \equiv |x_1^m \cdots x_{n_e}^m\rangle$ as defined in Eq. (6.8) and define the projection operator

$$\hat{x}^m = \hat{x}_1 \cdots \hat{x}_{n_e},$$

where $\hat{x}_i$ is equal to $\hat{n}_{x_i\uparrow}$ if $i \leq N_\uparrow$ or $\hat{n}_{x_i\downarrow}$ otherwise. It follows that

$$\hat{x}^m\,|\phi_n\rangle = \delta_{nm}|\phi_n\rangle$$

and therefore the Jastrow operator

$$\hat{J} = e^{-\sum_o \gamma_o \hat{x}^o}$$

maps $|\Phi\rangle$ unto $|\Psi\rangle$

$$\begin{aligned} |\Psi\rangle &= \hat{J}\,|\Phi\rangle \\ &= \sum_m e^{-\gamma_m} g(x^m)|\phi_m\rangle. \end{aligned} \tag{6.17}$$

We have established that the expansion coefficients, for a given ground state wave function have the same sign and hence, since no physical property depends on the sign of the wave function, we can choose a common sign for the $f(x^m)$ and $g(x^m)$. The Jastrow factors, γ_m, are well defined and real.

$\hat{J}$ is hermitian but not unitary. The inverse of $\hat{J}$,

$$\hat{J}^{-1} = e^{\sum_o \gamma_o \hat{x}^o}.$$

The correlation energy in terms of the Jastrow factors

The time independent Schrödinger equation for the ground state of the interacting Hubbard Hamiltonian $\hat{H}$ (Eq. (6.1)) can be written as

$$\hat{H}\hat{J}\left|\Phi\right\rangle = E\hat{J}\left|\Phi\right\rangle.$$

Operating from the right with $\hat{J}^{-1}$ leads to

$$\hat{J}^{-1}\hat{H}\hat{J}\left|\Phi\right\rangle = E\left|\Phi\right\rangle.$$

$\hat{J}$ commutes with $\hat{u}$ and $\hat{v}$, which leads to

$$\left(\hat{J}^{-1}\hat{T}\hat{J} + \hat{u} + \hat{v}\right)\left|\Phi\right\rangle = E\left|\Phi\right\rangle. \tag{6.18}$$

The transcorrelated Hamiltonian [85] $\hat{J}^{-1}\hat{T}\hat{J} + \hat{u} + \hat{v}$ is not hermitian since $\hat{J}$ is not unitary. It cannot be used in a variational form since the eigenspectrum is not bounded from below and the eigenenergies can be complex. Acting on Eq. (6.18) with $\langle\Phi|$ and recalling that $E^{Hx}[\rho] = \langle\Phi\left|\hat{u}\right|\Phi\rangle$, we have

$$\langle\Phi|\,\hat{J}^{-1}\hat{T}\hat{J}\left|\Phi\right\rangle + E^{Hx}[\rho] + \langle\rho v\rangle = E[\rho].$$

Since

$$E[\rho] = T^{KS}[\rho] + E^c[\rho] + E^{Hx}[\rho] + \langle\rho v\rangle \tag{6.19}$$

it follows that

$$\begin{aligned} E^c[\rho] &= \langle\Phi|\,\hat{J}^{-1}\hat{T}\hat{J}\left|\Phi\right\rangle - \langle\Phi|\,\hat{T}\left|\Phi\right\rangle \\ &= \langle\Phi|\,\hat{J}^{-1}\hat{T}\hat{J} - \hat{T}\left|\Phi\right\rangle. \end{aligned} \tag{6.20}$$

This is an expression for the correlation energy as an expectation value of an operator with respect to the KS ground state wave function. It is an appealing expression, but unfortunately the unknowns have simply been shifted to the Jastrow operator. If the Jastrow factors γ_m are known, we can calculate the interacting system ground state energy from Eq. (6.20).

The total and correlation energies can be expressed as

$$E[\rho] = -t\sum_{m,m'} g(x^m)\sum_{i=1}^{n_e}\sum_{s=\pm1} g(x^{m\prime}(x_i^{m\prime}+s)\equiv x^m)e^{-\gamma_{x^{m\prime}}}e^{\gamma_{x^m}} + \langle\Phi[v_{ks}]|\,(\hat{u}+\hat{v})\,|\Phi[v_{ks}]\rangle, \tag{6.21}$$

$$E^c[\rho] = -t\sum_{m,m'} g(x^m)\sum_{i=1}^{n_e}\sum_{s=\pm1} g(x^{m\prime}(x_i^{m\prime}+s)\equiv x^m)\left(e^{-\gamma_{x^{m\prime}}}e^{\gamma_{x^m}} - 1\right). \tag{6.22}$$

Details of the derivations can be found in Appendix C.

6.3 Jastrow factors and Numerical correlation energies

In this section we apply the expression for the correlation energy derived in Section 6.2.2 in numerical verification. We calculate the correlation energy for a four site lattice, and validate the expression for the correlation energy.

Let us start by recalling the relationships:

$$f(x^m) = e^{-\gamma_{x^m}} g(x^m)$$

expressed in Eq. (6.16). It implies that

$$\gamma_{x^m} = \log\Big(\frac{g(x^m)}{f(x^m)}\Big),$$

and this gives the exact Jastrow factors γ_m. We solve the Schrödinger equation for the one dimensional Hubbard Hamiltonian directly and then numerically determine the corresponding KS potential. In Figures 6.1 and 6.3, we plot $e^{-\gamma_m}$ of the exact Jastrow factors as function of m, the indices of the basis functions ϕ_m. There are many potential wave functions that can yield the same density. It is interesting to observe that the relative weights of the two sets of expansion coefficients follow a similar pattern, though, not surprisingly, the coefficients are not the same for the two wave functions. The green left-facing-triangle and the blue circle solid lines in Figures 6.2 and 6.4 represent respectively the KS and the interacting weights. Some KS weights are smaller and some larger than the interacting weights. This is reflected in the Jastrow factors as well.

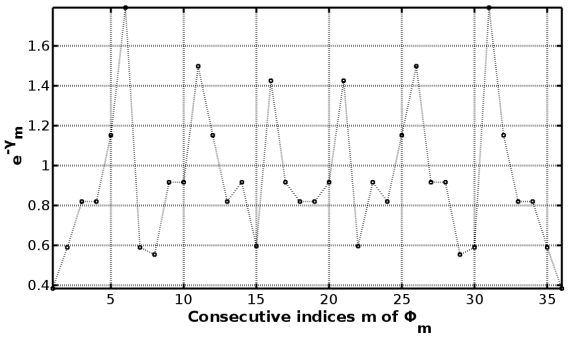


Figure 6.1: Variation of γ_m against the indices m for $n_e = 4$.

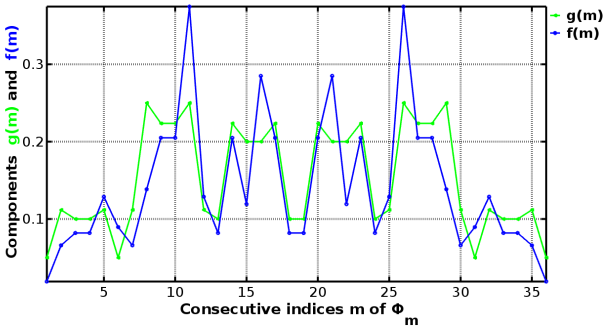


Figure 6.2: Variation of g and f against the indices m for $n_e = 4$.

The exact correlation energy is calculated using Eq. (6.22). The correlation energy determined from the definition and from the Jastrow factor expression, are identical, as expected. For a given n_e, the correlation energy is computed from the KS ground state wave function and the Jastrow factors. So, while varying the number of electrons, we gradually evaluated E^c. Figure 6.5, upon n_e, shows the variation of the exact correlation energy when the interaction term is set to 2. The correlation energy is negative, as it should be from definition, and becomes considerable at half filling. The value at half filling remains higher while looking at the behaviour of the exact correlation energy with respect to the interaction term. This is plotted in Figure 6.6. The shape evolves upwards from the black cross-hair

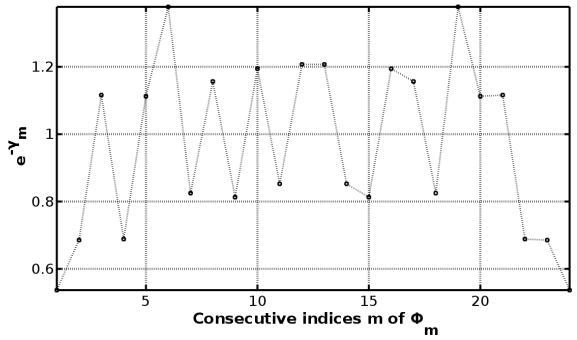


Figure 6.3: Variation of γ_m against the indices m for $n_e = 5$.

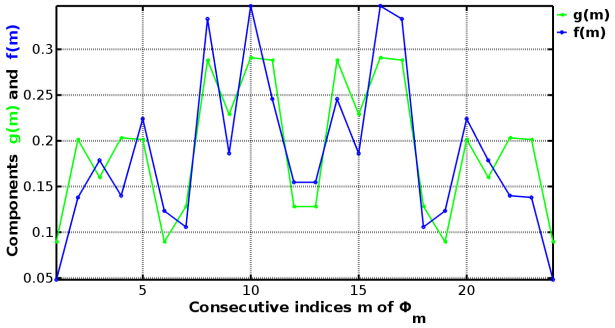


Figure 6.4: Variation of g and f against the indices m for $n_e = 5$.

solid lines at the bottom to the horizontal blue downward-facing-triangle solid line while u_o varies from -2 to 0 whereas it evolves downwards from the horizontal to the bottom red cross dotted lines when u_0 increases fro 0 to 2. Therefore, $|E^c|$ increases with $|u_0|$ while vanishing for $n_e = 0,\ 1,\ 7,\ 8$.

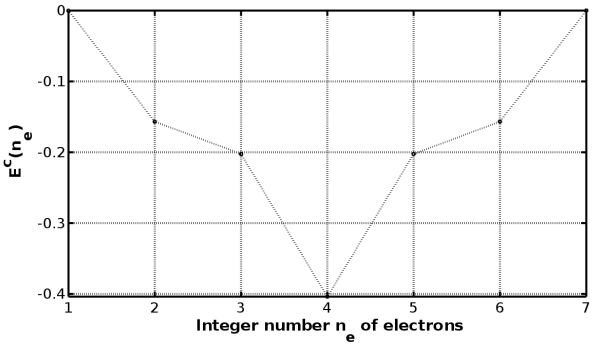


Figure 6.5: Variation of E^c against the number of electrons n_e for a 4 site lattice where $t = 1$, $u_o = 2$ and $v = 1$.

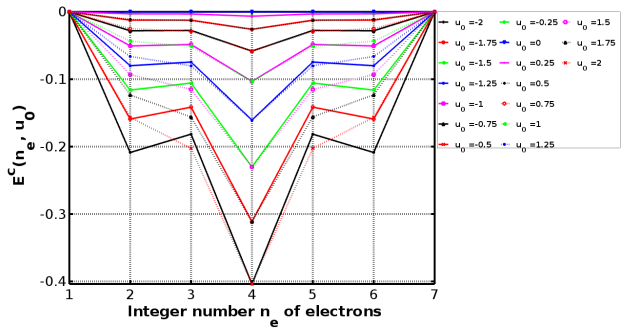


Figure 6.6: Variation of E^c against the number of electrons $n_e \in [1, 7] \cap \mathbb{N}$ and $u_o \in [-2, 2] \cap \frac{\mathbb{N}}{2}$ for a 4 site lattice.

It is worthy to point out that the plots in Figures 6.5 and 6.6 are only linear interpolations of the correlation energy between two integer particle numbers; otherwise, the intermediate values are worked out by using the ensemble DFT techniques (see Section 2.4.1). The results from the two methods are highlighted in Figure 6.7. It turns out that the ensemble correlation energy is continuous at integer particle numbers as expected; but, it is not linear between integers. A simple interpolation fails to exhibit this property of the correlation energy. However, within this section, we only consider the linear interpolation because so far, the Jastrow factors method concerns lattice with integer particle number. In the ensemble formulation, the total energy interpolates linearly and, since the charge density is linear in the particle number, the potential energy term also interpolates linearly The components of the energy decomposition, kinetic, Hartree+exchange and correlation energies, on the other hand, are not required to interpolate linearly, only the sum of these terms must interpolate linearly.

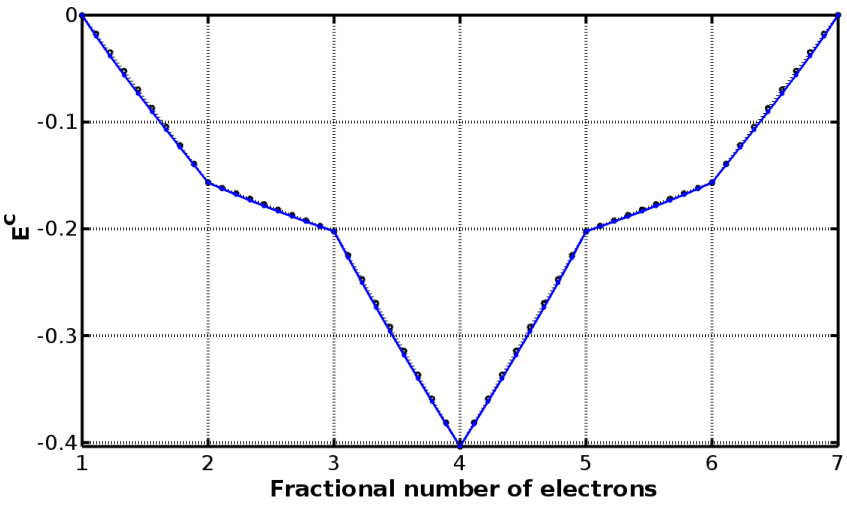


Figure 6.7: Variation of E^c against the number of electrons, n_e, for a 4 site lattice with $t = 1$, $u_o = 2$ and $v_i = 1$, $\forall i$. The black shape represents the correlation energy linearly interpolated between integers and the blue colour shapes the ensemble correlation energy.

6.4 Correlation potential

In this section an expression for the correlation potential is derived in terms of the Jastrow factors.

The correlation term, defined as

$$\begin{aligned} E^c[\rho] &= \langle\Psi|\hat{T}+\hat{u}|\Psi\rangle - \langle\Phi|\hat{T}+\hat{u}|\Phi\rangle \\ &= \langle\Phi|\hat{J}^{-1}\hat{T}\hat{J}-\hat{T}|\Phi\rangle, \end{aligned} \tag{6.23}$$

and the Hartree+exchange term, given by

$$E^{Hx} = \langle\Phi|\hat{u}|\Phi\rangle, \tag{6.24}$$

are implicit functionals of the ground state density. From the Hohenberg-Kohn theorems we know that two external potentials that differ by more than a constant will generate different ground state densities. If we know what a ground state density is, we can formally search through the space of all possible potentials for the one that generates the density of interest. We can do this for the interacting as well as the noninteracting systems. In principle we can use the corresponding Hamiltonian and then find the ground state wave function. Once we have the wave function we can calculate the correlation and exchange energies by taking the expectation values of $\hat{T}+\hat{u}$ and $\hat{u}$ according to Eqs.(6.23)) and (6.24). This is not a practical way of finding the exchange and correlation energies, but it illustrates what we mean by an 'implicit' functional. We have a formal algorithm to get the energies from the density, but there is no expression in terms of the density that we can manipulate to get the energies of the functional derivatives.

Here we are interested in site density derivatives $\frac{dE^c[\rho]}{d\rho_i}$ and $\frac{dE^{Hx}[\rho]}{d\rho_i}$, but, as outlined above, we do not have a convenient expression in terms of the density to work with. We do know how to change the wave functions as a functional of the external potential. We use the chain rule which allows us to express $\frac{dE^c[\rho]}{d\rho_i}$ as

$$\frac{dE^c[\rho]}{d\rho_i} = \sum_{j=1}^{L} \frac{dE^c[\rho]}{dv_j^{KS}} \frac{dv_j^{KS}}{d\rho_i}, \tag{6.25}$$

and a similar expression for $\frac{dE^{Hx}[\rho]}{d\rho_i}$. This approach requires that we calculate $\frac{dv_j^{KS}}{d\rho_i}$, which cannot be done directly, but we can calculate $\frac{d\rho_i}{dv_j^{KS}}$ and then take the inverse. We used this approach when we examined the Hartree+exchange approximation. For the correlation term,

$$E^c[\rho] = \langle\Phi|\,\hat{J}^{-1}\hat{T}\hat{J} - \hat{T}\,|\Phi\rangle\,,$$

this approach is complicated by the Jastrow operator since a direct evaluation of $\frac{dE^c[\rho]}{dv_k^{KS}}$ will require determining $\frac{d\hat{J}}{dv_k^{KS}}$.

In Section 6.2.2 we introduced the Jastrow factor which maps the KS ground state wave function onto the corresponding interacting system ground state wave function

$$|\Psi\rangle = \hat{J}\,|\Phi\rangle\,. \tag{6.26}$$

We are interested in DFT, but the mapping of the ground state wave function onto an interacting particle ground state wave function can be generalised to any convenient independent particle ground state wave function. Consider an independent particle Hubbard Hamiltonian

$$\hat{H}^s = \hat{T} + \hat{v}^s,$$

where $\hat{v}^s$ is an arbitrary single particle potential. We require that the ground state eigenfunction of $\hat{H}^s$ is anti-symmetric under the exchange of particle coordinates to retain the Fermionic nature of the wave function, but $\hat{v}^s$ can be any single particle potential. For simplicity we also require that $\hat{v}^s$ is multiplicative.

Let

$$\hat{H}^s\,|\Phi^s\rangle = E^s\,|\Phi^s\rangle$$

define the ground state solution of $\hat{H}^s$. The ground state density of $\hat{H}^s$ will coincide with the interacting particle ground state density ρ only when $\hat{v}^s = v^{KS}[\rho]$. We can expand $|\Phi^s\rangle$ in terms of basis functions $|\phi_n\rangle$ as before. Since the properties of the expansion coefficients are determined by the kinetic energy operator, the expansion coefficients of $|\Phi^s\rangle$ will all be non-zero and all have the same sign. The ground state is also non-degenerate. For a chosen interacting system, we define a Jastrow operator $\hat{J}[v^s,\rho]$ which maps an arbitrary $|\Phi^s[v^s]\rangle$ onto a fixed interacting ground state wave function $|\Psi\rangle$,

$$\begin{aligned} |\Psi[\rho]\rangle &= \hat{J}[v^s,\rho]\,|\Phi^s[v^s]\rangle \\ &= \sum e^{-\gamma^s_{x^m}} g^s(x^m)|\phi_m\rangle. \end{aligned} \tag{6.27}$$

$\hat{J}[v^s,\rho]$, depends on v^s, through $\Phi^s[v^s]$, and ρ, through $|\Psi[\rho]\rangle$. We can also define a general expression for the interacting energy. The expression

$$\left(\hat{J}^{-1}[v^s,\rho]\,\hat{T}\hat{J}[v^s,\rho] + \hat{u} + \hat{v}\right)|\Phi^s[v^s]\rangle = E[\rho]\,|\Phi^s[v^s]\rangle \tag{6.28}$$

is satisfied for an arbitrary v^s. The interacting system energy can be expressed as

$$E[\rho] = \langle\Phi^s[v^s]|\,\hat{J}^{-1}[v^s,\rho]\,\hat{T}\hat{J}[v^s,\rho]\,|\Phi^s[v^s]\rangle + \langle\Phi^s[v^s]|\,\hat{u}\,|\Phi^s[v^s]\rangle + \langle\rho^s v\rangle\,, \tag{6.29}$$

where ρ^s is the ground state density of $\hat{H}^s$. The Hartree+exchange energy

$$E^{Hx}[\rho^s] = \langle\Phi[v^s]\,|\hat{u}|\,\Phi[v^s]\rangle$$

is a functional of the ground state density, ρ^s (or v^s). $\langle\Phi^s[v^s]|\,\hat{J}^{-1}[v^s,\rho]\,\hat{T}\hat{J}[v^s,\rho]\,|\Phi^s[v^s]\rangle$,on the other hand, depends on ρ^s and ρ.

The energy of the interacting system can be expressed as

$$E\left[\rho\right]=T^{KS}\left[\rho^{s}\right]+\tilde{E}^{c}\left[v^{s},\rho\right]+E^{Hx}\left[\rho^{s}\right]+\left\langle \rho^{s}v\right\rangle ,\tag{6.30}$$

where the generalized correlation energy, $\tilde{E}^{c}\left[\rho^{s}\right]$, is given by

$$\tilde{E}^{c}\left[v^{s},\rho\right]=\left\langle \Phi\left[v^{s}\right]\right|\left(\hat{J}^{-1}\left[v^{s},\rho\right]\hat{T}\hat{J}\left[v^{s},\rho\right]-\hat{T}\right)\left|\Phi\left[v^{s}\right]\right\rangle .\tag{6.31}$$

At the solution point, when $v^{s}=v^{KS}$, $\tilde{E}^{c}\left[v^{s},\rho\right]=E^{c}\left[\rho\right]$, but away from the solution point it has a more general meaning. In Eq. (6.30) the only terms on the right-hand side with information about the many-particle system are $\tilde{E}^{c}\left[v^{s},\rho\right]$ and $\left\langle \rho^{s}v\right\rangle$. $\tilde{E}^{c}\left[v^{s},\rho\right]$, as defined above, is defined for ρ, a ground state density of the interacting system with external potential v. This implies that we cannot take the functional derivative on the right of Eq. (6.30) for fixed v, we have to take into account the dependence of v on ρ. Formally the full functional derivative of $E\left[\rho\right]$ with respect to ρ is equal the functional derivative of $\tilde{E}^{c}\left[v^{s},\rho\right]+\left\langle \rho^{s}v\right\rangle$ with respect to ρ at fixed v^{s},

$$\begin{aligned}\frac{\delta E\left[\rho\right]}{\delta\rho} &= \frac{\delta\tilde{E}^{c}\left[v^{s},\rho\right]}{\delta\rho}+\left\langle \rho^{s}\frac{\delta v}{\delta\rho}\right\rangle \\ &= \frac{\delta T^{KS}\left[\rho\right]}{\delta\rho}+v^{c}\left[\rho\right]+v^{Hx}\left[\rho\right]+v+\left\langle \rho\frac{\delta v}{\delta\rho}\right\rangle ,\end{aligned}$$

where the last line follows from the known expression for $E\left[\rho\right]$ as a functional of ρ (and v):

$$E\left[\rho\right]=T^{KS}\left[\rho\right]+E^{c}\left[\rho\right]+E^{HX}\left[\rho\right]+\left\langle \rho v\right\rangle .$$

At the solution point, comparison of the last two equations shows that

$$\begin{aligned}\left.\frac{\delta\tilde{E}^{c}\left[v^{s},\rho\right]}{\delta\rho}\right|_{v^{s}=v^{KS}\left[\rho\right]} &= \frac{\delta T^{KS}\left[\rho\right]}{\delta\rho}+v^{c}\left[\rho\right]+v^{HX}\left[\rho\right]+v \\ &= \mu,\end{aligned}$$

where μ is the chemical potential. It follows that $\left.\frac{\delta\tilde{E}^{c}\left[v^{s},\rho\right]}{\delta\rho}\right|_{v^{s}}$, taken at fixed v^{s} is not the correlation potential. We can understand why this is the case. $\left.\frac{\delta\tilde{E}^{c}\left[v^{s},\rho\right]}{\delta\rho}\right|_{v^{s}}$ is a 'partial' functional derivative. If we use the full functional derivative, $\frac{\delta\tilde{E}^{c}\left[v^{KS}\left[\rho\right],\rho\right]}{\delta\rho}$, where $v^{KS}\left[\rho\right]$ as a functional of ρ, we recover the correlation potential as it can be seen from Eq. (6.30). This, however, will require that we work with a restricted set of densities that are simultaneously v and v^{KS} representable [36, 86, 87].

We can still derive an expression for v^{c} from $\tilde{E}^{c}\left[v^{s},\rho\right]$ by considering its dependence on v^{s} at fixed ρ. In the discussion below, we keep ρ constant unless explicitly stated. For convenience of notation, from here on we shall suppress the dependence of $\tilde{E}^{c}\left[v^{s},\rho\right]$ and $\hat{J}\left[v^{s},\rho\right]$ on ρ and the dependence of the expansion coefficients g on v^{s}.

Since $E\left[\rho\right]$ is independent of v^{s}, Eq. (6.29) implies that

$$\frac{d}{dv_{k}^{s}}\left\langle \Phi\left[v^{s}\right]\right|J^{-1}\left[v^{0}\right]\hat{T}J\left[v^{s}\right]\left|\Phi\left[v^{s}\right]\right\rangle +\frac{d}{dv_{k}^{s}}\left\langle \Phi\left[v^{s}\right]\right|\left(\hat{u}+\hat{v}\right)\left|\Phi\left[v^{s}\right]\right\rangle =0,$$

and Eq. (6.31) implies that

$$\frac{d}{dv_{k}^{s}}\left(T^{KS}\left[v^{s}\right]+\tilde{E}^{c}\left[v^{s}\right]\right)=-\frac{d}{dv_{k}^{s}}\left\langle \Phi\left[v^{s}\right]\right|\hat{v}\left|\Phi\left[v^{s}\right]\right\rangle -\frac{d}{dv_{k}^{s}}E^{Hx}\left[v^{s}\right].$$

With

$$\begin{aligned}\frac{d}{dv_{k}^{s}}\left\langle \Phi\left[v^{s}\right]\right|\hat{v}\left|\Phi\left[v^{s}\right]\right\rangle &= \frac{d}{dv_{k}^{s}}\left\langle \Phi\left[v^{s}\right]\right|\sum_{j\sigma}v_{j}\hat{n}_{j\sigma}\left|\Phi\left[v^{s}\right]\right\rangle \\ &= \sum_{j}v_{j}\frac{d\rho_{j}^{s}}{dv_{k}^{s}},\end{aligned}$$

one obtains

$$\frac{d\tilde{E}^c\left[v^s\right]}{dv_k^s} = -\sum_j v_j \frac{d\rho_j^s}{dv_k^s} - \frac{d}{dv_k^s} E^{Hx}\left[v^s\right] - \frac{d}{dv_k^s} T^{KS}\left[v^s\right]. \tag{6.32}$$

In contrast to $\tilde{E}^c\left[\rho, v_s\right]$, $E^{Hx}\left[v^s\right] \equiv E^{Hx}\left[\rho^s\right]$ is a functional of ρ^s only and therefore

$$\left.\frac{\delta E^{Hx}\left[\rho^s\right]}{\delta \rho^s}\right|_{\rho^s} = v^{Hx}\left[\rho^s\right],$$

the Hartree+exchange potential at density ρ^s. At solution p/oint, $v^s = v^{KS}$,

$$\begin{aligned}
\left.\frac{d\tilde{E}^c\left[v^s\right]}{dv_k^s}\right|_{v^s=v^{KS}} &= -\sum_j v_j \left.\frac{d\rho_j}{dv_k^s}\right|_{v^s=v^{KS}} - \sum_j v_j^{Hx} \left.\frac{d\rho_j}{dv_k^s}\right|_{v^s=v^{KS}} + \sum_j v_j^{KS} \left.\frac{d\rho_j}{dv_k^s}\right|_{v^s=v^{KS}} \\
&= \sum_j v_j^c \left.\frac{d\rho_j}{dv_k^s}\right|_{v^s=v^{KS}}
\end{aligned}$$

since $v_j^{KS}\left[\rho\right] = v_j\left[\rho\right] + v_j^{Hx}\left[\rho\right] + v_j^c\left[\rho\right]$. In other words, at the solution point,

$$\left.\frac{d\tilde{E}^c\left[v^s\right]}{dv_k^s}\right|_{v^s=v^{KS}} = \frac{dE^c\left[\rho\right]}{dv_k^{KS}},$$

and we can use $\left.\frac{d\tilde{E}^c[v^s]}{dv_k^s}\right|_{v^s=v^{KS}}$ in Eq. (6.25) to evaluate v^c. Away from the solution point, $\frac{d\tilde{E}^c[v^s]}{dv_k^s}$, is not a DFT correlation potential.

In Appendix C we show how to evaluate $\frac{de^{-\gamma_x n}}{dv_k^s}$, which provides us with a computation framework to calculate $\frac{d\tilde{E}^c[v^s]}{dv_k^s}$. We can, however, find an expression for $\frac{d\tilde{E}^c[v^s]}{dv_k^s}$ while avoiding calculating $\frac{dJ[v^s]}{dv_k^s}$. Since $E\left[\rho\right]$ is independent of v^s by definition, taking the derivative with respect to v_k^s of Eq. (6.28) gives

$$\frac{d\left(\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\right)}{dv_k^s}\left|\Phi^s\left[v^s\right]\right\rangle + \left(\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right] + \hat{u} + \hat{v}\right)\left|\frac{d}{dv_k^s}\Phi^s\left[v^s\right]\right\rangle = E\left[\rho\right]\left|\frac{d}{dv_k^s}\Phi^s\left[v^s\right]\right\rangle.$$

Acting from the left with $\left\langle\Phi\left[v^s\right]\right|$ leads to

$$\left\langle\Phi\left[v^s\right]\right|\frac{d\left(\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\right)}{dv_k^s}\left|\Phi\left[v^s\right]\right\rangle = -\left\langle\Phi\left[v^s\right]\right|\left(\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right] + \hat{u} + \hat{v}\right)\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle \tag{6.33}$$

since $\left|\Phi\left[v^s\right]\right\rangle$ is real and normalised. We can now write

$$\begin{aligned}
&\frac{d}{dv_k^s}\left\langle\Phi\left[v^s\right]\right|\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\left|\Phi\left[v^s\right]\right\rangle \\
= &\left\langle\frac{d}{dv_k^s}\Phi\left[v^s\right]\right|\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\left|\Phi\left[v^s\right]\right\rangle + \left\langle\Phi\left[v^s\right]\right|\frac{d\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]}{dv_k^s}\left|\Phi\left[v^s\right]\right\rangle \\
&+ \left\langle\Phi\left[v^s\right]\right|\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle.
\end{aligned} \tag{6.34}$$

Combining Eqs. (6.33) and (6.34), we find that

$$\begin{aligned}
&\frac{d}{dv_k^s}\left\langle\Phi\left[v^s\right]\right|\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\left|\Phi\left[v^s\right]\right\rangle \\
= &\left\langle\frac{d}{dv_k^s}\Phi\left[v^s\right]\right|\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\left|\Phi\left[v^s\right]\right\rangle - \left\langle\Phi\left[v^s\right]\right|\left(\hat{u}+\hat{v}\right)\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle.
\end{aligned} \tag{6.35}$$

Finally we arrive at an expression for $\frac{d\tilde{E}^c[v^s]}{dv_k^s}$:

$$\begin{aligned}\frac{d\tilde{E}^c\left[v^s\right]}{dv_k^s} &= \frac{d}{dv_k^s}\left\langle\Phi\left[v^s\right]\right|\left(\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\right)\left|\Phi\left[v^s\right]\right\rangle - \frac{d}{dv_k^s}\left\langle\Phi\left[v^s\right]\right|\hat{T}\left|\Phi\left[v^s\right]\right\rangle \\ &= \left\langle\Phi\left[v^s\right]\right|\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right]\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle - \left\langle\Phi\left[v^s\right]\right|\left(\hat{u}+\hat{v}\right)\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle \\ &\quad -2\left\langle\Phi\left[v^s\right]\right|\hat{T}\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle \\ &= \left\langle\Phi\left[v^s\right]\right|\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right] - 2\hat{T}\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle - \left\langle\Phi\left[v^s\right]\right|\left(\hat{u}+\hat{v}\right)\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle. \end{aligned} \tag{6.36}$$

This expression is in terms of independent particle ground state wave function and its derivative with respect to the independent system potential as well as the Jastrow operator. This is a promising expression. $\frac{d}{dv_k^s}\left|\Phi\left[v^s\right]\right\rangle$ can be determined from perturbation theory, which leaves the problem of determining the Jastrow factor.

Taking into account that

$$\begin{aligned}\left\langle\Phi\left[v^s\right]\right|\left(\hat{u}+\hat{v}\right)\frac{d}{dv_k^s}\left|\Phi\left[v^s\right]\right\rangle &= \tfrac{1}{2}\tfrac{d}{dv_k^s}\left\langle\Phi\left[v^s\right]\right|\left(\hat{u}+\hat{v}\right)\left|\Phi\left[v^s\right]\right\rangle \\ &= \tfrac{1}{2}\tfrac{d}{dv_k^s}E^{Hx}\left[\rho^s\right] + \tfrac{1}{2}\left\langle\tfrac{d\rho^s}{dv_k^s}\hat{v}\right\rangle\end{aligned}$$

and (see Appendix C for details)

$$\begin{aligned}&\left\langle\Phi\left[v^s\right]\right|\left(\hat{J}^{-1}\left[v^s\right]\hat{T}\hat{J}\left[v^s\right] - 2\hat{T}\right)\left|\frac{d}{dv_k^s}\Phi\left[v^s\right]\right\rangle \\ = \; & -t\sum_{m,m\prime}\frac{dg\left(x^m\right)}{dv_k^s}\sum_{i=1}^{n_e}\sum_{s=\pm1} g(x^{m\prime}(x_i^{m'}+s)\equiv x^m)\left(e^{-\gamma_{x^{m\prime}}\left[v^s\right]}e^{\gamma_{x^m}\left[v^s\right]}-2\right),\end{aligned}$$

we can write the generalized exchange potential

$$\tilde{v}_k^c\left[v^s\right] = \frac{d\tilde{E}^c\left[v^s\right]}{d\rho_k^s}$$

as (6.37)

$$\begin{aligned}\tilde{v}_k^c\left[v^s\right] &= \sum_{o=1}^{L}\frac{d\tilde{E}^c\left[v^s\right]}{dv_o^s}\frac{dv_o^s}{d\rho_k^s} \\ &= -t\sum_{o=1}^{L}\sum_{m,m\prime}\frac{dg\left(x^m\right)}{dv_o^s}\sum_{i=1}^{n_e}\sum_{s=\pm1} g(x^{m\prime}(x_i^{m'}+s)\equiv x^m)\left(e^{-\gamma_{x^{m\prime}}\left[v^s\right]}e^{\gamma_{x^m}\left[v^s\right]}-2\right)\frac{dv_o^s}{d\rho_k^s} \\ &\quad -\frac{1}{2}v_k^{Hx}\left[\rho^s\right] - \frac{1}{2}v_k.\end{aligned} \tag{6.37}$$

At the solution point, where

$$v^s = v^{KS},$$

$$\tilde{v}_k^c\left[v^{KS}\right] = v_k^c\left[\rho\right].$$

In contrast to $v_k^{Hx}\left[\rho^s\right]$, which, as shown in Chapter 5, can be found from the properties of the noninteracting system only, $\tilde{v}_k^c\left[v^s\right]$ depends on $\gamma_{x^{m\prime}}\left[v^s\right]$, which links the interacting and noninteracting systems.

It is interesting to note, from comparing the derivative of Eq. (6.31) and Eq. (6.37), that

$$\begin{aligned} 4t\sum_{m} g\left(x^{m}\right)\sum_{i=1}^{N}\sum_{s=\pm 1} g(x^{m\prime}(x_i^{m^{\prime}}+s) &\equiv x^{m})\frac{d}{dv_k^s}\left(e^{-\gamma_{x^{m\prime}}[v^s]}e^{\gamma_{x^m}[v^s]}\right) \\ &= v_k^{Hx}\left[\rho^s\right]+v_k, \end{aligned}$$

which relates parameters that depend on the interacting system, $\gamma_{x^m}\left[v^s\right]$, and quantities that are only related to the noninteracting system, $g\left(x^m\right)$ and $v_k^{Hx}\left[\rho^s\right]$. This can be used as a check on the veracity of the $\gamma_{x^{m\prime}}\left[v^s\right]$ since $v_k^{Hx}\left[\rho^s\right]$ can be determined independently.

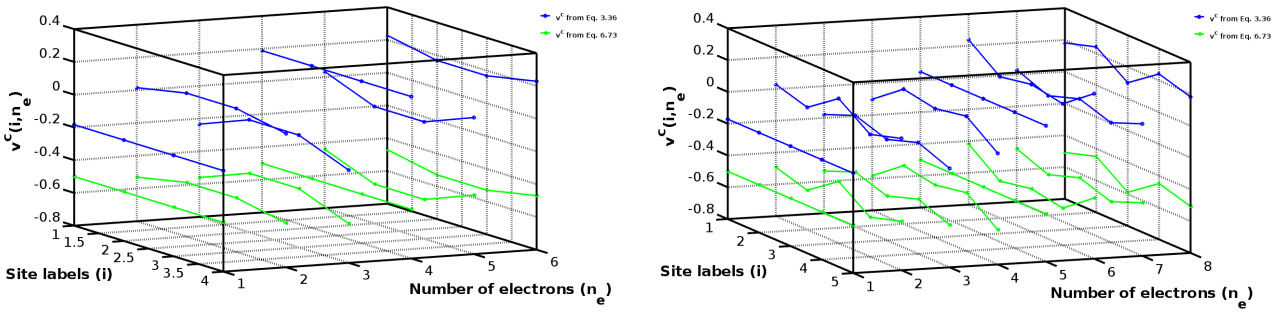
6.5 Numerical examples for the correlation potential

This Section follows the numerical investigation of the correlation energy in Section 6.3. We furthered our investigation in the electrons correlation. Here, we focus on the correlation potential which was formally and explicitly deduced in terms of the noninteracting ground state, the Jastrow factor, the Hartree+exchange potential and the external potential.

Upon Eq. (6.37),

$$\begin{aligned} v_k^c\left[\rho\right] &= -t\sum_{o=1}^{L}\sum_{m,m\prime}\frac{dg\left(x^m\right)}{dv_o^s}\sum_{i=1}^{n_e}\sum_{s=\pm 1} g(x^{m\prime}(x_i^{m^{\prime}}+s)\equiv x^m)\left(e^{-\gamma_{x^{m\prime}}[v^s]}e^{\gamma_{x^m}[v^s]}-2\right)\frac{dv_o^s}{d\rho_k^s} \\ &\quad -\frac{1}{2}v_k^{Hx}\left[\rho^s\right]-\frac{1}{2}v_k, \end{aligned}$$

an algorithm is coded to numerically calculate the correlation potential. For comparison purposes, we also computed the exact correlation potential (Eq. (3.16)) by solving the noninteracting system. Since, potentials are defined up to a constant shift, we found it necessary to set the value of the correlation potentials at the first lattice site to zero while comparing both potentials. We notice that, the error is zero up to the tolerance we have fixed for numerical calculations. So, once the Jastrow factors are well approximated, the correlation potential follows as well. This is pictured in Figures 6.8a and 6.8b where the green left-facing-triangle and the blue circle solid lines are used to draw correlation potentials obtained respectively from Eqs.(3.16) and (6.37).



(a) (b)

Figure 6.8: Variation of v^c against integer number, n_e, of electrons for a 4 (a) and a 5 (b) site lattice where $t=1$, $u_o=2$ and $v=1$.

6.6 Computational scheme for a self-consistent DFT calculation

At this point we abandon the hope of finding an analytical expression for the exchange and correlation energies as functionals of the ground state densities. An alternative to solve the problem of finding the energy and density of the interacting system using analytic expressions is to construct a self-consistent computational scheme that will give as the interacting system ground state density and energy while all calculations are done within the framework of a Kohn-Sham noninteracting particle fictitious system. In the previous sections we showed that it is possible to construct an expression for the Hartree+exchange and correlation energy and potential that gives us the desired energies and potential if we have the Jastrow parameters. We still need a way to update the Jastrow factors if we hope to construct a self-consistent scheme.

In Appendix (C), Eq. (C.13), we show that the Jastrow factors γ_{x^n} satisfy the expression

$$e^{\gamma_{x^n}} = \frac{g^s\left(x^n\right)\left\langle x^n\right| E_s^\gamma - (\hat{u}+\hat{v})\left|x^n\right\rangle}{-t\sum_{i=1}^{n_e}\sum_{s=\pm 1} g^s(x^n(x_i^n+s))e^{-\gamma_{x^n(x_i^n+s)}}}, \tag{6.38}$$

where at the solution point $E_s^\gamma = E\left[\rho\right]$, the interacting ground state energy. For a set of Jastrow parameters E^γ can be expressed according to Eq. (6.29). In this expression the $g^s\left(x^n\right)$ are the expansion coefficients of the ground state wave function of the noninteracting system with potential v^s. According to Eq. (6.29) we can express E^γ in terms of the Jastrow factors and the noninteracting ground state wave function.

We have expressions for the correlation and Hartree+exchange potentials that can be updated in each self-consistent cycle till convergence is achieved. Instead of following the conventional approach of updating the Hartree+exchange and correlation potentials in a self-consistent cycle, we have an alternative. We are looking for a noninteracting particle potential that yields the same density as the interacting system density ρ. We can write the site densities

$$\rho_i = \sum e^{-2\gamma^s_{x^n}} g_s^2\left(x^n\right)\left\langle x^n\right|\hat{n}_{i\uparrow}+\hat{n}_{i\downarrow}\left|x^n\right\rangle \tag{6.39}$$

and

$$\rho_i^s = \sum g_s^2\left(x^n\right)\left\langle x^n\right|\hat{n}_{i\uparrow}+\hat{n}_{i\downarrow}\left|x^n\right\rangle. \tag{6.40}$$

Both the $\gamma^s_{x^n}$ and $g_s\left(x^n\right)$ are functions of the site potentials v_i^s. At the solution point, $v_i^s = v_i^{KS}$ and $\rho_i = \rho_i^s = \rho_i^{KS}$. We can calculate

$$\frac{d\left(\rho_i-\rho_i^s\right)}{dv_k^s} = C_{ik}$$

and then, using a linear approximation, set

$$\rho_i - \rho_i^s + \sum_k C_{ik}\Delta v_k^s = 0. \tag{6.41}$$

This gives a linear set of equations with general solution

$$\Delta v^s = C^{-1}\left(\rho^s-\rho\right). \tag{6.42}$$

Here

$$C_{ik} = \frac{d}{dv_k^s}\sum\left(e^{-2\gamma^s_{x^n}}-1\right) g_s^2\left(x^n\right)\left\langle x^n\right|\hat{n}_{i\uparrow}+\hat{n}_{i\downarrow}\left|x^n\right\rangle,$$

which can be determined as outlined in Appendix C and D and where we derive expressions for the derivatives of $e^{-\gamma^s_{x^n}}$ and $g_s^2\left(x^n\right)$ with respect to v_k^s. We can use Eq. (6.42) to update the Kohn-Sham potential in each cycle till convergence is reached. Eq. (6.42) assumes that C^{-1} exists. In the cycle where C^{-1} does not exist, we can update the diagonal terms in Eq. (6.41) or use a singular value decomposition of C in the update of that cycle.

6.7 Conclusion

By introducing the Jastrow factors, we were able to express the correlation energy and potential and the Hartree+exchange energy density functionals as functions of the Jastrow factors. The numerical results showed that the approximations are exact. We find that this approach works well and we can reproduce the exact interacting energy and density while working only within a fictitious noninteracting particle framework.

Chapter 7

Summary and Conclusion

In this project we examined Density Functional Theory within an ensemble formulation on a lattice. The single chain Hubbard model we used can be solved numerically by direct diagonalisation for a finite number of sites and the uniform infinite chain can be solved using the Bethe ansatz. We examined the existence of the derivative discontinuity of the exchange correlation potential for the exact system and showed that in the ensemble formulation a discontinuity in the exchange-correlation potential is ensured for any approximation. We examined a simple uniform exchange correlation approximation and a Hartree+exchange correlation approximation where the correlation energy term is neglected and found that both approximations reproduce the trends of the exact formalism as a function of particle number. However, the approximations do not consistently perform at the same level of accuracy and may not reproduce all features of the real system under all circumstances.

In Kohn-Sham DFT the formal barrier to an exact solution of the Kohn-Sham system is the complexity of the correlation term. The kinetic and exchange energies can be solved exactly within the independent particle Kohn-Sham framework since by definition these terms are formulated as functionals of the Kohn-Sham system. The formal definition of the Kohn-Sham DFT correlation energy makes direct reference to the interacting ground state wave function. Approximations of the correlation energy, despite the fact that the correlation energy normally contributes a small component to the total energy, have performed poorly. Instead of examining approximations to the correlation energy, in the the final part of the project, we introduced a new mapping of the independent particle system onto the interacting system. We use the same set of basis functions for the expansion of the ground state wave functions of the interacting and noninteracting systems and simply map the noninteracting system expansion coefficients onto the expansion coefficients of the interacting system. With this mapping we were able to derive a set of expressions that can be used in a self-consistent approach within the noninteracting particle framework. This was the original goal of the Kohn-Sham formulation.

We implemented this approach for small systems to demonstrate that it works. The formalism is general, but it is particularly well suited to the single band Hubbard model with nearest neighbour hopping because of the properties of the system. The spin operator commutes with the Hamiltonian which allows a selection of basis functions for the expansions. For positive t the expansion coefficients are all non-zero and all have the same sign, and the ground states are non-degenerate. These three properties make the implementation of our approach relatively simple.

Future work includes a general formulation of the approach which may be complicated by changes in the sign of the coefficients, coefficients may be zero for the noninteracting system expansion and the ground states may be non-degenerate.

The manner in which we solved the problem of the noninteracting system uses a many-particle set of basis functions. All final calculations were performed in the noninteracting particle framework, but with a many-particle set of basis functions. We illustrated that it is possible to solve the Kohn-Sham equations exactly, but the approach does not immediately lend itself to finding the ground state solution of a long chain Hubbard system since the independent particle Hamiltonian increases in size as fast as the interacting particle Hamiltonian. However, the independent many-particle Hamiltonian can be solved in a single particle picture from which the many-particle ground state wave function can be constructed and then expanded in terms of the same basis functions used in this project. The derivatives with respect to the site potentials can also be done at the single particle level and assembled as derivatives of the expansion coefficients of the many-particle basis functions. That will allow us to tackle much larger systems.

In conclusion, the major contribution of the project was the first formulation which allows an exact solution of the ground state energy wave function of simple model of interacting particles, while doing all calculations for a fictitious noninteracting particle system. It is a first exact implementation of the original idea of Kohn and Sham to use the principles of density functional theory and map the interacting system onto a noninteracting system which yields the same density as the interacting system

Appendix A

Derivation of Hartree, and Hartree-Fock and Thomas-Fermi methods

A.1 Hartree equations

The components of the Hamiltonian $\hat{H}$, defined in Eq. (2.15), can be detailed as follows

$$\begin{aligned}\hat{T} &= \hat{T}_e \\ &= -\frac{\hbar^2}{2m}\sum_i^{n_e}\nabla_{r_i}^2 \\ &= \sum_i^{n_e}\hat{T}_i,\end{aligned}$$

$$\begin{aligned}\hat{u} &= \frac{1}{2}\sum_{i\neq j}^{n_e}\frac{e^2}{4\pi\epsilon}\frac{1}{\mid r_j - r_i \mid} \\ &= \frac{1}{2}\sum_{i\neq j}^{n_e}\hat{u}(r_i, r_j)\end{aligned}$$

and

$$\begin{aligned}\hat{v} = \hat{v}_{n-e} &= \sum_{i=1}^{n_e}\sum_{j=1}^{m} -\frac{e^2}{4\pi\epsilon}\frac{Z_j}{\mid R_j - r_i \mid} \\ &= \sum_{i=1}^{n_e}\hat{v}(r_i).\end{aligned}$$

Indeed, Eq. (2.18) used in Section 2.2.1 stems from:

$$\begin{aligned}\langle\delta_i\phi \mid \hat{H}\phi\rangle &= \langle\varphi_1(\mathbf{x}_1)\cdots\varphi_{i-1}(\mathbf{x}_{i-1})\delta_i\varphi_i(\mathbf{x}_i)\varphi_{i+1}(\mathbf{x}_{i+1})\cdots\varphi_{n_e}(\mathbf{x}_{n_e}) \mid \hat{H}\varphi_1(\mathbf{x}_1)\cdots\varphi_{n_e}(x_{n_e})\rangle \\ &= \langle\delta\varphi_i(\mathbf{x}_i) \mid \hat{H}(\mathbf{x}_i)\varphi_i(\mathbf{x}_i)\rangle\prod_{j\neq i}\langle\varphi_j \mid \varphi_j\rangle + \sum_{k\neq i}\langle\varphi_k(\mathbf{x}_k) \mid \hat{H}(\mathbf{x}_k)\varphi_k(\mathbf{x}_k)\rangle\langle\delta\varphi_i \mid \varphi_i\rangle\prod_{j\neq i,k}\langle\varphi_j \mid \varphi_j\rangle \\ &= \langle\delta\varphi_i(\mathbf{x}_i) \mid \hat{H}(\mathbf{x}_i)\varphi_i(\mathbf{x}_i)\rangle \\ &= \epsilon_i\langle\delta\varphi_i(\mathbf{x}_i) \mid \varphi_i(\mathbf{x}_i)\rangle \\ &= \epsilon_i\langle\delta_i\phi \mid \phi\rangle.\end{aligned}$$

Let us substitute in Eq. (2.18), $\hat{H}$ by its expression used in Eq. (2.15). This yields

$$\Big\langle \delta_k\phi_0 \Big| \hat{T}\phi_0 \Big\rangle + \langle \delta_k\phi_0 \,|\hat{u}\phi_0\,\rangle + \langle \delta_k\phi_0 \,|\hat{v}\phi_0\,\rangle = \epsilon_k \langle \delta\varphi_k \mid \varphi_k\rangle$$

$$\sum_i^{n_e}\Big[\Big\langle \delta_k\phi_0 \Big| \hat{T}_i\phi_0 \Big\rangle + \langle \delta_k\phi_0 \,|\hat{v}(\mathbf{r}_i)\phi_0\,\rangle \Big] + \frac{1}{2}\sum_{i,j,i\neq j}^{n_e} \langle \delta_k\phi_0 \,|\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\phi_0\,\rangle = \epsilon_k \langle \delta\varphi_k \mid \varphi_k\rangle.$$

We have

$$\begin{aligned}\sum_i^{n_e} \Big\langle \delta_k\phi_0 \Big| \hat{T}_i\phi_0 \Big\rangle &= \sum_{i,i\neq k}^{n_e}\Big[\prod_{j,j\notin\{i,k\}}^{n_e} \langle \varphi_j\,|\varphi_j\,\rangle\Big]\,\langle \delta\varphi_k\,|\varphi_k\,\rangle\,\langle \varphi_i^\dagger(\mathbf{x}_i)\hat{T}_i\varphi_i(\mathbf{x}_i)\rangle \\ &\quad + \Big[\prod_{j,j\neq k}^{n_e} \langle \varphi_j\,|\varphi_j\,\rangle\Big]\langle \delta\varphi_k^\dagger(\mathbf{x}_k)\hat{T}_k\varphi_k(\mathbf{x}_k)\rangle \\ &= \langle \delta\varphi_k^\dagger(\mathbf{x}_k)\hat{T}_k\varphi_k(\mathbf{x}_k)\rangle,\end{aligned}$$

$$\begin{aligned}\sum_i^{n_e} \langle \delta\phi_0\,|\hat{v}(\mathbf{r}_i)\phi_0\,\rangle &= 0 + \Big[\prod_{j,j\neq k}^{n_e} \langle \varphi_j\,|\varphi_j\,\rangle\Big]\langle \delta\varphi_k^\dagger(\mathbf{x}_k)\hat{v}(r_k)\varphi_k(\mathbf{x}_k)\rangle \\ &= \langle \delta\varphi_k^\dagger(\mathbf{x}_k)\hat{v}(\mathbf{r}_k)\varphi_k(\mathbf{x}_k)\rangle,\end{aligned}$$

and

$$\begin{aligned}\sum_{i,j,i<j}^{n_e} \langle \delta_k\phi_0\,|\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\phi_0\,\rangle &= \frac{1}{2}\sum_{\substack{i,j,i\neq j\\ i\neq k, j\neq k}}^{n_e}\Big[\prod_{s\notin\{i,j,k\}}^{n_e} \langle \varphi_s\,|\varphi_s\,\rangle\Big]\,\langle \delta\varphi_k\,|\varphi_k\,\rangle\,\langle \varphi_j^\dagger(\mathbf{x}_j)\varphi_i^\dagger(\mathbf{x}_i)\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_i(\mathbf{x}_i)\varphi_j(\mathbf{x}_j)\rangle \\ &\quad + \sum_{i,i\neq k}^{n_e}\Big[\prod_{s\notin\{i,k\}}^{n_e} \langle \varphi_s\,|\varphi_s\,\rangle\Big]\langle \delta\varphi_k^\dagger(\mathbf{x}_k)\varphi_i^\dagger(\mathbf{x}_i)\hat{u}(\mathbf{r}_i,\mathbf{r}_k)\varphi_i(\mathbf{x}_i)\varphi_k(\mathbf{x}_k)\rangle \\ &= \sum_{i,i\neq k}^{n_e} \langle \delta\varphi_k^\dagger(\mathbf{x}_k)\varphi_i^\dagger(\mathbf{x}_i)\hat{u}(\mathbf{r}_i,\mathbf{r}_k)\varphi_i(\mathbf{x}_i)\varphi_k(\mathbf{x}_k)\rangle \\ &= \langle \delta\varphi_k^\dagger(\mathbf{x}_k)\Big[\sum_{i,i\neq k}^{n_e} \varphi_i^\dagger(\mathbf{x}_i)\hat{u}(\mathbf{r}_i,\mathbf{r}_k)\varphi_i(\mathbf{x}_i)\Big]\varphi_k(\mathbf{x}_k)\rangle \\ &= \langle \delta\varphi_k^\dagger(\mathbf{x}_k)\hat{v}_H(\mathbf{x}_k)\varphi_k(\mathbf{x}_k)\rangle.\end{aligned}$$

Finally,

$$\langle \delta\varphi_k^\dagger(\mathbf{x}_k)\hat{T}_k\varphi_k(\mathbf{x}_k) + \delta\varphi_k^\dagger(\mathbf{x}_k)\Big[\sum_{i,i\neq k}^{n_e} \varphi_i^\dagger(\mathbf{x}_i)\hat{u}(\mathbf{r}_i,\mathbf{r}_k)\varphi_i(\mathbf{x}_i)\Big]\varphi_k(\mathbf{x}_k) + \delta\varphi_k^\dagger(\mathbf{x}_k)\hat{v}(\mathbf{r}_k)\varphi_k(\mathbf{x}_k)\rangle = \epsilon_k\langle \delta\varphi_k \mid \varphi_k\rangle \quad \text{(A.1)}$$

$$\langle \delta\varphi_k^\dagger(\mathbf{x}_k)\Big(\hat{T}_k + \langle\Big[\sum_{i,i\neq k}^{n_e} \varphi_i^\dagger(\mathbf{x}_i)\hat{u}(\mathbf{r}_i,\mathbf{r}_k)\varphi_i(\mathbf{x}_i)\Big]\rangle_{\mathbf{r}_i} + \hat{v}(\mathbf{r}_k)\Big)\varphi_k(\mathbf{x}_k)\rangle_{r_k} = \epsilon_k\langle \delta\varphi_k \mid \varphi_k\rangle \quad \text{(A.2)}$$

$$\langle \delta\varphi_k^\dagger(\mathbf{x}_k)\Big(\hat{T}_k + \hat{v}_H(\mathbf{r}_k) + \hat{v}(\mathbf{r}_k)\Big)\varphi_k(\mathbf{x}_k)\rangle = \epsilon_k\langle \delta\varphi_k \mid \varphi_k\rangle. \quad \text{(A.3)}$$

Since Eq. (A.3) holds for all possible variation δ and all $k \in [1, n_e]\cap\mathbb{N}$, it gives up the single-electron Schrödinger equation

$$\Big(\hat{T}_k + \hat{v}^H(r_k) + \hat{v}(r_k)\Big)\varphi_k = \epsilon_k\varphi_k$$

with the universal functional

$$F^H[\varphi] = \langle \varphi^\dagger(\mathbf{x})\Big(\hat{T} + \hat{v}^H(\mathbf{r})\Big)\varphi(\mathbf{x})\rangle.$$

A.2 Hartree-Fock Method

As it is defined in Eq. (2.24), a Slater determinant is an anti-symmetric wave function since

$$\phi(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_j,\cdots,\mathbf{x}_i,\cdots,\mathbf{x}_{n_e}) = \frac{1}{\sqrt{n_e!}}\det\begin{pmatrix} \varphi_1(\mathbf{x}_1) & \cdots & \varphi_i(\mathbf{x}_1) & \cdots & \varphi_j(\mathbf{x}_1) & \cdots & \varphi_{n_e}(\mathbf{x}_1) \\ \vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \vdots \\ \varphi_1(\mathbf{x}_j) & \cdots & \varphi_i(\mathbf{x}_j) & \cdots & \varphi_j(\mathbf{x}_j) & \cdots & \varphi_{n_e}(\mathbf{x}_j) \\ \vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \vdots \\ \varphi_1(\mathbf{x}_i) & \cdots & \varphi_i(\mathbf{x}_i) & \cdots & \varphi_j(\mathbf{x}_i) & \cdots & \varphi_{n_e}(\mathbf{x}_i) \\ \vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \vdots \\ \varphi_1(\mathbf{x}_{n_e}) & \cdots & \varphi_i(\mathbf{x}_j) & \cdots & \varphi_j(\mathbf{x}_i) & \cdots & \varphi_{n_e}(\mathbf{x}_{n_e}) \end{pmatrix},$$

$$= -\frac{1}{\sqrt{n_e!}}\det\begin{pmatrix} \varphi_1(\mathbf{x}_1) & \cdots & \varphi_i(\mathbf{x}_1) & \cdots & \varphi_j(\mathbf{x}_1) & \cdots & \varphi_{n_e}(\mathbf{x}_1) \\ \vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \vdots \\ \varphi_1(\mathbf{x}_i) & \cdots & \varphi_i(\mathbf{x}_i) & \cdots & \varphi_j(\mathbf{x}_i) & \cdots & \varphi_{n_e}(\mathbf{x}_i) \\ \vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \vdots \\ \varphi_1(\mathbf{x}_j) & \cdots & \varphi_i(\mathbf{x}_j) & \cdots & \varphi_j(\mathbf{x}_j) & \cdots & \varphi_{n_e}(\mathbf{x}_j) \\ \vdots & \cdots & \cdots & \cdots & \cdots & \cdots & \vdots \\ \varphi_1(\mathbf{x}_{n_e}) & \cdots & \varphi_i(\mathbf{x}_j) & \cdots & \varphi_j(\mathbf{x}_i) & \cdots & \varphi_{n_e}(\mathbf{x}_{n_e}) \end{pmatrix},$$

$$= -\phi(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_i,\cdots,\mathbf{x}_j,\cdots,\mathbf{x}_{n_e}).$$

An alternative definition of the Slater determinant is

$$\phi(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_i,\cdots,\mathbf{x}_j,\cdots,\mathbf{x}_{n_e}) = \sum_\theta \frac{(-1)^{\varepsilon_\theta}}{\sqrt{n_e!}}\varphi_{\theta(1)}(\mathbf{x}_1)\varphi_{\theta(2)}(\mathbf{x}_2)\cdots\varphi_{\theta(n_e)}(\mathbf{x}_{n_e}). \tag{A.4}$$

In Eq. (A.4), θ is any permutation of $\{1,2,\cdots,n_e\}$ and ε_θ is its signature or more precisely the number of time θ permutes the elements of the ordered set $\{1,2,\cdots,n_e\}$. The product

$$\varphi_{\theta(1)}(\mathbf{x}_1)\varphi_{\theta(2)}(\mathbf{x}_2)\cdots\varphi_{\theta(n_e)}(\mathbf{x}_{n_e})$$

is also called a single-Slater determinant. We shall see now what is new when one uses the Slater determinant in Eq. (2.18). We first compute the variation of the kinetic energy with respect to the k^{th} single-electron wave function as follows

$$\begin{aligned}
\sum_i^{n_e}\left\langle \delta_k\phi_0 \left| \hat{T}_i\phi_0 \right.\right\rangle &= \sum_i^{n_e}\left\langle \delta_k\sum_\theta \frac{(-1)^{\varepsilon_\theta}}{\sqrt{n_e!}}\varphi_{\theta(1)}\varphi_{\theta(2)}\cdots\varphi_{\theta(n_e)}\left|\hat{T}_i\right|\sum_{\theta'}\frac{(-1)^{\varepsilon_{\theta'}}}{\sqrt{n_e!}}\varphi_{\theta'(1)}\varphi_{\theta'(2)}\cdots\varphi_{\theta'(n_e)}\right\rangle \\
&= \sum_i^{n_e}\sum_{\theta,\theta'}\frac{(-1)^{\varepsilon_\theta+\varepsilon_{\theta'}}}{n_e!}\Big[\prod_{j,\theta(j)\neq k}^{n_e}\left\langle\varphi_{\theta(j)}\left|\varphi_{\theta'(j)}\right.\right\rangle\Big]\left\langle\delta\varphi_k^\dagger(\mathbf{x}_i)\hat{T}_i\varphi_{\theta'(i)}(\mathbf{x}_i)\right\rangle \\
&= \sum_i^{n_e}\sum_{\substack{\theta\\ \theta(i)=k}}\frac{(-1)^{2\varepsilon_\theta}}{n_e!}\left\langle\delta\varphi_k^\dagger(\mathbf{x}_i)\hat{T}_i\varphi_k(\mathbf{x}_i)\right\rangle \\
&= \sum_i^{n_e}\frac{1}{n_e!}(n_e-1)!\left\langle\delta\varphi_k^\dagger(\mathbf{x}_i)\hat{T}_i\varphi_k(\mathbf{x}_i)\right\rangle \\
&= \frac{1}{n_e}\sum_i^{n_e}\left\langle\delta\varphi_k^\dagger(\mathbf{x})\hat{T}_r\varphi_k(\mathbf{x})\right\rangle \text{ since the index } i \text{ is a dummy variable} \\
&= \left\langle\delta\varphi_k^\dagger(\mathbf{x})\hat{T}_r\varphi_k(\mathbf{x})\right\rangle.
\end{aligned} \tag{A.5}$$

Repeating the same process for the external potential energy,

$$\begin{aligned}
\sum_i^{n_e} \langle \delta\phi_0 \,|\hat{v}(\mathbf{r}_i)\phi_0\rangle &= \sum_i^{n_e} \left\langle \delta_k \sum_\theta \frac{(-1)^{\varepsilon_\theta}}{\sqrt{n_e!}} \varphi_{\theta(1)}\varphi_{\theta(2)}\cdots\varphi_{\theta(n_e)} \,|\hat{v}_i| \sum_{\theta'} \frac{(-1)^{\varepsilon_{\theta'}}}{\sqrt{n_e!}} \varphi_{\theta'(1)}\varphi_{\theta'(2)}\cdots\varphi_{\theta'(n_e)} \right\rangle \\
&= \sum_i^{n_e}\sum_{\theta,\theta'} \frac{(-1)^{\varepsilon_\theta+\varepsilon_{\theta'}}}{n_e!} \Big[\prod_{j\neq i}^{n_e} \langle \varphi_{\theta(j)} \,|\varphi_{\theta'(j)}\rangle \Big] \left\langle \delta\varphi_k^\dagger(\mathbf{x}_i)\hat{v}_i\varphi_{\theta'(i)}(\mathbf{x}_i) \right\rangle \\
&= \sum_i^{n_e}\sum_\theta \frac{1}{n_e!} \left\langle \delta\varphi_k^\dagger(\mathbf{x}_i)\hat{v}_i\varphi_k(\mathbf{x}_i) \right\rangle \\
&= \frac{1}{n_e}\sum_i^{n_e} \left\langle \delta\varphi_k^\dagger(\mathbf{x}_i)\hat{v}_i\varphi_k(\mathbf{x}_i) \right\rangle,
\end{aligned}$$

one reaches

$$\sum_i^{n_e} \langle \delta_k\phi_0 \,|\hat{v}(\mathbf{r}_i)\phi_0\rangle = \left\langle \delta_k\varphi_k^\dagger(\mathbf{x})\hat{v}_{\mathbf{r}}\varphi_k(\mathbf{x}) \right\rangle. \tag{A.6}$$

We are now left with the variation of the coulomb potential energy:

$$\begin{aligned}
\sum_{i,j,i<j}^{n_e} \langle \delta_k\phi_0 \,|\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\phi_0\rangle = \frac{1}{2}\sum_{i,j,i\neq j}^{n_e}\sum_{\theta,\theta'} \frac{(-1)^{\varepsilon_\theta+\varepsilon_{\theta'}}}{n_e!} \Big[\prod_{s\notin\{i,j\}}^{n_e} \langle \varphi_{\theta(s)} \,|\varphi_{\theta'(s)}\rangle \Big] \\
\times \left\langle \delta\varphi_{\theta(i)}^\dagger(\mathbf{x}_i)\varphi_{\theta(j)}^\dagger(\mathbf{x}_j)\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta'(j)}(\mathbf{x}_j)\varphi_{\theta'(i)}(\mathbf{x}_i) \right\rangle.
\end{aligned}$$

Only the braket products that involve $\theta(i) = k$ or $\theta(j) = k$ will contribute to the summation. Thus,

$$\begin{aligned}
\sum_{i,j,i<j}^{n_e} \langle \delta_k\phi_0 \,|\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\phi_0\rangle &= \frac{1}{2}\sum_{i,j,j\neq i}^{n_e} \sum_{\substack{\theta,\theta' \\ \theta(s)=\theta'(s) \\ s\notin\{i,j\}}} \frac{(-1)^{\varepsilon_\theta+\varepsilon_{\theta'}}}{n_e!} \langle \delta[\varphi_{\theta(i)}^\dagger(\mathbf{x}_i)\varphi_{\theta(j)}^\dagger(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta'(j)}(\mathbf{x}_j)\varphi_{\theta'(i)}(\mathbf{x}_i)\rangle \\
&= \frac{1}{2}\sum_{i,j,j\neq i}^{n_e}\sum_\theta \frac{1}{n_e!} \langle \delta[\varphi_{\theta(i)}^\dagger(\mathbf{x}_i)\varphi_{\theta(j)}^\dagger(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(j)}(\mathbf{x}_j)\varphi_{\theta(i)}(\mathbf{x}_i)\rangle \\
&+ \frac{1}{2}\sum_{i,j,j\neq i}^{n_e}\sum_\theta \frac{-1}{n_e!} \langle \delta[\varphi_{\theta(i)}^\dagger(\mathbf{x}_i)\varphi_{\theta(j)}^\dagger(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(i)}(\mathbf{x}_j)\varphi_{\theta(j)}(\mathbf{x}_i)\rangle.
\end{aligned} \tag{A.7}$$

Let us rewrite the two terms of Eq. (A.7) independently of the permutation θ. Let E_H and E_x be two potential energies satisfying

$$\delta_k E_H = \frac{1}{2}\sum_{i,j,j\neq i}^{n_e}\sum_\theta \frac{1}{n_e!} \langle \delta[\varphi_{\theta(i)}^\dagger(\mathbf{x}_i)\varphi_{\theta(j)}^\dagger(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(j)}(\mathbf{x}_j)\varphi_{\theta(i)}(\mathbf{x}_i)\rangle$$

and

$$\delta_k E_x = -\frac{1}{2}\sum_{i,j,j\neq i}^{n_e}\sum_\theta \frac{1}{n_e!} \langle \delta[\varphi_{\theta(i)}^\dagger(\mathbf{x}_i)\varphi_{\theta(j)}^\dagger(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(i)}(\mathbf{x}_j)\varphi_{\theta(j)}(\mathbf{x}_i)\rangle$$

respectively. One has,

$$\begin{aligned}
\delta_k E_H &= \frac{1}{2}\sum_{i,j,j\neq i}^{n_e}\sum_{\theta}\frac{1}{n_e!}\langle\delta_k[\varphi^\dagger_{\theta(i)}(\mathbf{x}_i)\varphi^\dagger_{\theta(j)}(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(j)}(\mathbf{x}_j)\varphi_{\theta(i)}(\mathbf{x}_i)\rangle \\
&= \frac{1}{2}\sum_{i,j,j\neq i}^{n_e}\sum_{\theta}\frac{1}{n_e!}(n-2)!\langle\delta_k[\varphi^\dagger_{\theta(i)}(\mathbf{x}_i)\varphi^\dagger_{\theta(j)}(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(j)}(\mathbf{x}_j)\varphi_{\theta(i)}(\mathbf{x}_i)\rangle \\
&= \frac{1}{2n_e(n_e-1)}\sum_{i,j,j\neq i}^{n_e}\sum_{\theta}\langle\delta_k[\varphi^\dagger_{\theta(i)}(\mathbf{x}_i)\varphi^\dagger_{\theta(j)}(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(j)}(\mathbf{x}_j)\varphi_{\theta(i)}(\mathbf{x}_i)\rangle \\
&= \frac{1}{2n_e(n_e-1)}\sum_{i,j,i\neq j}^{n_e}\sum_{\substack{\theta\\ \theta(i)=k}}\langle\delta_k[\varphi^\dagger_{\theta(i)}(\mathbf{x}_i)\varphi^\dagger_{\theta(j)}(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(j)}(\mathbf{x}_j)\varphi_k(\mathbf{x}_i)\rangle \\
&= \sum_{\substack{m,n,m\neq n\\ k\notin\{n,m\}}}^{n_e}\frac{1}{2n_e(n_e-1)}\sum_{i,j,i\neq j}^{n_e}\langle\delta_k[\varphi^\dagger_n(\mathbf{x})\varphi^\dagger_m(\mathbf{x}')]\hat{u}(\mathbf{r},\mathbf{r}')\varphi_m(\mathbf{x}')\varphi_n(\mathbf{x})\rangle \\
&= \sum_{m,m\neq k}^{n_e}\langle\delta\varphi^\dagger_k(\mathbf{x})\varphi^\dagger_m(\mathbf{x}')\hat{u}(\mathbf{r},\mathbf{r}')\varphi_m(\mathbf{x}')\varphi_k(\mathbf{x})\rangle \\
&= \langle\delta\varphi^\dagger_k(\mathbf{x})\Big[\sum_{m,m\neq k}^{n_e}\varphi^\dagger_m(\mathbf{x}')\hat{u}(\mathbf{r},\mathbf{r}')\varphi_m(\mathbf{x}')\Big]\varphi_k(\mathbf{x})\rangle \\
&= \langle\delta_k\varphi^\dagger_k(\mathbf{x})\hat{v}^H(\mathbf{r})\varphi_k\mathbf{x})\rangle,
\end{aligned} \tag{A.8}$$

and

$$\begin{aligned}
\delta_k E_x &= \frac{1}{2}\sum_{i,j,j\neq i}^{n_e}\sum_{\theta}\frac{-1}{n_e!}\langle\delta_k[\varphi^\dagger_{\theta(i)}(\mathbf{x}_i)\varphi^\dagger_{\theta(j)}(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_{\theta(i)}(\mathbf{x}_j)\varphi_{\theta(j)}(\mathbf{x}_i)\rangle \\
&= \sum_{\substack{n,m,m\neq n\\ k\in\{n,m\}}}\frac{-1}{2n_e(n_e-1)}\sum_{i,j,j\neq i}^{n_e}\langle\delta_k[\varphi^\dagger_n(\mathbf{x}_i)\varphi^\dagger_m(\mathbf{x}_j)]\hat{u}(\mathbf{r}_i,\mathbf{r}_j)\varphi_n(\mathbf{x}_j)\varphi_m(\mathbf{x}_i)\rangle \\
&= -\sum_{m,m\neq k}^{n_e}\langle\delta\varphi^\dagger_k(\mathbf{x})\varphi^\dagger_m(\mathbf{x}')\hat{u}(\mathbf{r},\mathbf{r}')\varphi_k(\mathbf{x}')\varphi_m(\mathbf{x})\rangle \\
&= -\langle\delta\varphi^\dagger_k(\mathbf{x})\sum_{m,m\neq k}^{n_e}\varphi^\dagger_m(\mathbf{x}')\hat{u}(\mathbf{r},\mathbf{r}')\varphi_k(\mathbf{x}')\varphi_m(\mathbf{x})\rangle \\
&= -\langle\delta\varphi^\dagger_k(\mathbf{x})\hat{v}^x[\mathbf{r},\mathbf{r}',\varphi_k]\rangle,
\end{aligned} \tag{A.9}$$

where $\hat{v}^x[\mathbf{r},\varphi_k]$ is the exchange potential. From all these results (Eqs. (A.5), (A.6), (A.8) and (A.9)) Eq. (2.18) yields

$$\Big[\hat{T}_\mathbf{r}+\hat{v}^H+\hat{v}^x[\varphi_k]+\hat{v}\Big]\varphi_k(\mathbf{x})=\epsilon_k\varphi_k(\mathbf{x})$$

which are the Hartree-Fock equations.

A.3 Thomas-Fermi equations

To highlight the work achieved by Thomas and Fermi, let us consider the phase space of the system. It is admitted that particles cannot move faster than light; therefore, in the momentum space, there exists a maximum momentum whose norm is less than mc where c is the speed of light. For any elementary volume $\Delta V_\mathbf{r}$ in the coordinate space, the maximum momentum exists and let $p_F(\mathbf{r})$ be its

norm. In the vicinity of $\mathbf{r}$, the momentum of all possible electrons is within the (momentum space) spheric volume

$$V_{\mathbf{p}} = \tfrac{4\pi}{3} p_F^3(\mathbf{r}). \tag{A.10}$$

The corresponding volume in the phase space is $\Delta V_{(\mathbf{r},\mathbf{p})} = V_{\mathbf{p}} \Delta V_{\mathbf{r}}$, that is

$$\Delta V_{(\mathbf{r},\mathbf{p})} = \tfrac{4\pi}{3} p_F^3(\mathbf{r}) \Delta V_{\mathbf{r}}. \tag{A.11}$$

It is a fact from the uncertainty principle that a volume of size h^3 (in the real space) contains as much as the number of particles allowed by Pauli exclusion principle. Since we have a system of electrons then only two electrons with opposite spins can be found in h^3. Therefore,

$$n_e = \frac{2}{h^3} \Delta V_{(\mathbf{r},\mathbf{p})} \tag{A.12}$$

is the fractional number of electrons within $\Delta V_{(\mathbf{r},\mathbf{p})}$. Substituting Eq. (A.11) into Eq. (A.12), it results

$$n_e = \tfrac{8\pi}{3h^3} p_F^3(\mathbf{r}) \Delta V_{\mathbf{r}}.$$

Willing to obtain a uniform density, one may consider

$$\rho(\mathbf{r}) = \frac{n_e}{\Delta V_{\mathbf{r}}}.$$

In other words, TF density is read as follows

$$\rho(\mathbf{r}) = \tfrac{8\pi}{3h^3} p_F^3(\mathbf{r}).$$

Conversely, one has

$$p_F(\mathbf{r}) = \Big(\frac{3h^3 \rho(\mathbf{r})}{8\pi}\Big)^{1/3},$$

which yields from a classical viewpoint the kinetic energy

$$\begin{aligned}
T^{TF} &= \int_{n_e} \frac{p^2}{2m_e} dn_e \\
&= \int_0^{p_F} \frac{p^2}{2m_e} d\Big(\frac{8\pi}{3h^3} p^3 \Delta V_{\mathbf{r}}\Big) \\
&= \Delta V_{\mathbf{r}} \int_0^{p_F} \frac{4\pi p^4}{m_e h^3} dp \\
&= \Delta V_{\mathbf{r}} \frac{4\pi}{5 m_e h^3} p_F^5(\mathbf{r}) \\
&= \Delta V_{\mathbf{r}} \frac{4\pi}{5 m_e h^3} \Big(\frac{3h^3 \rho(\mathbf{r})}{8\pi}\Big)^{5/3} \\
&= \Delta V_{\mathbf{r}} \frac{h^2}{m_e} \Big(\frac{3^{5/3}}{10(8\pi)^{2/3}}\Big) \rho(\mathbf{r})^{5/3} \\
&= \Delta V_{\mathbf{r}} \frac{h^2}{2^3 \pi^2 m_e} \Big(\frac{3^{5/3} \pi^{4/3}}{5}\Big) \rho(\mathbf{r})^{5/3} \\
&= \Delta V_{\mathbf{r}} \frac{\hbar^2}{2m_e} \kappa \rho(\mathbf{r})^{5/3} \text{ with } \kappa = \frac{\sqrt[3]{3^5 \pi^4}}{5},
\end{aligned} \tag{A.13}$$

the coulomb interaction potential energy

$$\begin{aligned}
U^{TF} &= \frac{e^2}{4\pi\epsilon} \int_{\Delta V_{\mathbf{r}}} \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}' \\
&= \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) \Big[\frac{e^2}{4\pi\epsilon} \int_{\Delta V_{\mathbf{r}}} \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r}'\Big] d\mathbf{r} \\
&= \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) v^{TF}(\mathbf{r}) d\mathbf{r}
\end{aligned}$$

and the external potential energy

$$E_v = \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}.$$

The expressions for the potential energies suggests the use of a kinetic energy density. In our case the density is

$$\rho_T = \frac{T^{TF}}{\Delta V_{\mathbf{r}}}.$$

Therefore, Eq. (A.13) implies

$$\rho_T(\mathbf{r}) = \frac{\hbar^2}{2m_e} \kappa \rho(\mathbf{r})^{5/3}$$

so that the kinetic energy becomes

$$\begin{aligned} T^{TF} &= \int_{\Delta V_{\mathbf{r}}} \rho_T(\mathbf{r}) d\mathbf{r} \\ &= \frac{\hbar^2}{2m_e} \kappa \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r})^{5/3} d\mathbf{r}. \end{aligned}$$

The total energy of the system as a functional of the uniform electronic density follows as

$$E^{TF} = \frac{\hbar^2}{2m_e} \kappa \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r})^{5/3} d\mathbf{r} + \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) v^{TF}(\mathbf{r}) d\mathbf{r} + \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}.$$

This leads to the TF universal functional

$$F^{TF} = \frac{\hbar^2}{2m_e} \kappa \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r})^{5/3} d\mathbf{r} + \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) v^{TF}(\mathbf{r}) d\mathbf{r}.$$

Since the ground state density minimizes the total energy under the constraint

$$\int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r}) d\mathbf{r} = n_e,$$

the following Lagrange multiplier equation holds

$$\delta_{(\rho,\mu)} \Big(E^{TF} - \mu \Big[\int \rho(\mathbf{r}) d\mathbf{r} - n_e \Big] \Big) \Big|_{\rho_0} = 0.$$

On one hand

$$\begin{aligned} \delta_\rho E^{TF} &= \frac{5\hbar^2}{6m_e} \kappa \int_{\Delta V_{\mathbf{r}}} \rho(\mathbf{r})^{2/3} \delta\rho d\mathbf{r} + \int_{\Delta V_{\mathbf{r}}} v^{TF}(\mathbf{r}) \delta\rho d\mathbf{r} + \int_{\Delta V_{\mathbf{r}}} v(\mathbf{r}) \delta\rho d\mathbf{r} \\ &= \int_{\Delta V_{\mathbf{r}}} \Big[\frac{5\hbar^2}{6m_e} \kappa \rho(\mathbf{r})^{2/3} + v^{TF}(\mathbf{r}) + v(\mathbf{r}) \Big] \delta\rho d\mathbf{r} \\ &= \int_{\Delta V_{\mathbf{r}}} \Big[\kappa' \rho(\mathbf{r})^{2/3} + v^{TF}(\mathbf{r}) + v(\mathbf{r}) \Big] \delta\rho d\mathbf{r} \text{ where } \kappa' = \frac{5\hbar^2}{6m_e} \kappa \end{aligned}$$

and on the other hand

$$\delta_\rho E^{TF} = \int_{\Delta V_{\mathbf{r}}} \mu \delta\rho d\mathbf{r}.$$

Thus,

$$\begin{aligned} \int_{\Delta V_{\mathbf{r}}} \Big[\kappa' \rho(\mathbf{r})^{2/3} + v^{TF}(\mathbf{r}) + v(\mathbf{r}) - \mu \Big] \delta\rho d\mathbf{r} = 0 \\ \kappa' \rho_0(\mathbf{r})^{2/3} + v^{TF}(\mathbf{r}) + v(\mathbf{r}) = \mu. \end{aligned}$$

Appendix B

Two site lattices described by the Hubbard Hamiltonian

Let us consider a single chain Hubbard model with a spin-independent external potential. To see how the different operators involved in the Hamiltonian take into account the physics that undergo the electrons, let us consider a two sites lattice with n_e electrons ($1 \leq n_e \leq 4$). The case $n_e = 2$ is relevant to point out the physics behind the Hubbard model. So, we will first consider two electron system and thereafter one.

B.1 Two sites with two electrons

B.1.1 Basis elements and the flip operator

The Hilbert space $\mathcal{H}_-^{\otimes 2}$ of the antisymmetric wave functions is generated by the vectors

$$\begin{aligned}
\phi_1 &= \hat{C}_{1\uparrow}^\dagger \hat{C}_{2\uparrow}^\dagger |\rangle, \\
\phi_2 &= \hat{C}_{1\uparrow}^\dagger \hat{C}_{1\downarrow}^\dagger |\rangle, \\
\phi_3 &= \hat{C}_{1\uparrow}^\dagger \hat{C}_{2\downarrow}^\dagger |\rangle, \\
\phi_4 &= \hat{C}_{2\uparrow}^\dagger \hat{C}_{1\downarrow}^\dagger |\rangle, \\
\phi_5 &= \hat{C}_{2\uparrow}^\dagger \hat{C}_{2\downarrow}^\dagger |\rangle
\end{aligned}$$

and

$$\phi_6 = \hat{C}_{1\downarrow}^\dagger \hat{C}_{2\downarrow}^\dagger |\rangle.$$

The wave functions ϕ_1 and ϕ_6 as well as ϕ_3 and ϕ_4 are similar through a flip of their spin states. Indeed, let $\hat{F}_{i\sigma}$ be the single-electron spin flip operator that changes at site i a spin σ electron into an electron with opposite spin σ'. This means,

$$\hat{F}_{i\sigma} = \hat{C}_{i\sigma'}^\dagger \hat{C}_{i\sigma}.$$

Since, for a given wave function all the spin states have to be flipped at once,

$$\begin{aligned}
\hat{F} &= \sum_{n_\uparrow=\max(0,n_e-L)}^{\min(n_e,L)} \sum_{1\le i_1<\cdots<i_{n_\downarrow}\le L} \sum_{1\le k_1<\cdots<k_{n_\uparrow}\le L} \prod_{j=\min(1,n_\downarrow)}^{n_\downarrow} \hat{F}_{i_j\downarrow} \prod_{j=\min(1,n_\uparrow)}^{n_\uparrow} \hat{F}_{k_j\uparrow} \\
&= \sum_{n_\uparrow=0}^{n_e} \sum_{1\le i_1<\cdots<i_{n_\downarrow}\le L} \sum_{1\le k_1<\cdots<k_{n_\uparrow}\le L} \prod_{j=\min(1,n_\downarrow)}^{n_\downarrow} \hat{F}_{i_j\downarrow} \prod_{j=\min(1,n_\uparrow)}^{n_\uparrow} \hat{F}_{k_j\uparrow} \\
&= \sum_{1\le k_1<k_2\le 2} \prod_{j=0}^{0} \hat{F}_{i_j\downarrow} \prod_{j=1}^{2} \hat{F}_{k_j\uparrow} + \sum_{1\le i_1\le 2} \sum_{1\le k_1\le 2} \prod_{j=1}^{1} \hat{F}_{i_j\downarrow} \prod_{j=1}^{1} \hat{F}_{k_j\uparrow} + \sum_{1\le i_1<i_2\le 2} \prod_{j=1}^{2} \hat{F}_{i_j\downarrow} \prod_{j=0}^{0} \hat{F}_{k_j\uparrow} \\
&= \sum_{1\le k_1<k_2\le 2} \hat{F}_{k_1\uparrow}\hat{F}_{k_2\uparrow} + \sum_{1\le i_1\le 2} \sum_{1\le k_1\le 2} \hat{F}_{i_1\downarrow}\hat{F}_{k_1\uparrow} + \sum_{1\le i_1<i_2\le 2} \hat{F}_{i_1\downarrow}\hat{F}_{i_2\downarrow} \\
&= \hat{F}_{1\uparrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\downarrow}
\end{aligned}$$

is the spin flip operator. Thereon,

$$\begin{aligned}
\hat{F}\phi_1 &= \Big(\hat{F}_{1\uparrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\downarrow}\Big)\phi_1 \\
&= \hat{F}_{1\uparrow}\hat{F}_{2\uparrow}\phi_1 \\
&= \hat{C}^\dagger_{1\downarrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= \hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= \hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}(1-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})(1-\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow})|\rangle \\
&= \hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}(1-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})(|\rangle-\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}|\rangle) \\
&= \hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}(1-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})|\rangle + |\rangle \\
&= \hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}(|\rangle-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}|\rangle) \\
&= \hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= \phi_6
\end{aligned}$$

and

$$\begin{aligned}
\hat{F}\phi_3 &= \Big(\hat{F}_{1\uparrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\downarrow}\Big)\phi_3 \\
&= \hat{F}_{2\downarrow}\hat{F}_{1\uparrow}\phi_3 \\
&= \hat{C}^\dagger_{2\uparrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}(1-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})(1-\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow})|\rangle \\
&= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}(1-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})|\rangle \\
&= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\
&= \phi_4.
\end{aligned}$$

On the other hand,

$$\begin{aligned}\hat{F}\phi_2 &= \Big(\hat{F}_{1\uparrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\downarrow}\Big)\phi_2 \\ &= \hat{F}_{1\downarrow}\hat{F}_{1\uparrow}\phi_2 \\ &= \hat{C}^\dagger_{1\uparrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\ &= \hat{C}^\dagger_{1\uparrow}(\hat{C}_{1\downarrow}\hat{C}^\dagger_{1\downarrow})(\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\uparrow})\hat{C}^\dagger_{1\uparrow}|\rangle \\ &= \hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\ &= \phi_2\end{aligned}$$

and

$$\begin{aligned}\hat{F}\phi_5 &= \Big(\hat{F}_{1\uparrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{1\uparrow} + \hat{F}_{2\downarrow}\hat{F}_{2\uparrow} + \hat{F}_{1\downarrow}\hat{F}_{2\downarrow}\Big)\phi_5 \\ &= \hat{F}_{2\downarrow}\hat{F}_{2\uparrow}\phi_5 \\ &= \hat{C}^\dagger_{2\uparrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\ &= \phi_5.\end{aligned}$$

It follows that

$$\hat{F}^2\phi_i = \phi_i.$$

B.1.2 The physics behind the kinetic operator and its properties

Let us denote by $\hat{t}_{ij\sigma}$ the operator $\hat{C}^\dagger_{j\sigma}\hat{C}_{i\sigma}$. The kinetic operator for the two electron system for a two site lattice takes the expression

$$\hat{T} = -t\hat{t}_{12\uparrow} - t\hat{t}_{21\uparrow} - t\hat{t}_{12\downarrow} - t\hat{t}_{21\downarrow}.$$

For instance, the action of $\hat{t}_{12\uparrow}$ on the basis elements gives

$$\begin{aligned}\hat{t}_{12\uparrow}\phi_1 &= \hat{C}^\dagger_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\ &= \hat{C}^\dagger_{2\uparrow}(1-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})\hat{C}^\dagger_{2\uparrow}|\rangle \\ &= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle - \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\ &= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle + \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}\hat{C}_{1\uparrow}|\rangle \\ &= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle + \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}(\hat{C}_{1\uparrow}|\rangle) \\ &= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\ &= |\rangle,\end{aligned}$$

$$\begin{aligned}\hat{t}_{12\uparrow}\phi_2 &= \hat{C}^\dagger_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\ &= \hat{C}^\dagger_{2\uparrow}(1-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})\hat{C}^\dagger_{1\downarrow}|\rangle \\ &= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle - \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\ &= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle + \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}(\hat{C}_{1\uparrow}|\rangle) \\ &= \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\ &= \phi_4,\end{aligned}$$

$$\begin{aligned}
\hat{t}_{12\uparrow}\phi_3 &= \hat{C}^{\dagger}_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^{\dagger}_{1\uparrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}(1-\hat{C}^{\dagger}_{1\uparrow}\hat{C}_{1\uparrow})\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle - \hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle + \hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{1\uparrow}\hat{C}^{\dagger}_{2\downarrow}(\hat{C}_{1\uparrow}|\rangle) \\
&= \hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= \phi_5,
\end{aligned}$$

$$\begin{aligned}
\hat{t}_{12\uparrow}\phi_4 &= \hat{C}^{\dagger}_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{1\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}(-\hat{C}^{\dagger}_{2\uparrow}\hat{C}_{1\uparrow})\hat{C}^{\dagger}_{1\downarrow}|\rangle \\
&= -\hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^{\dagger}_{1\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{1\downarrow}(\hat{C}_{1\uparrow}|\rangle) \\
&= |\rangle,
\end{aligned}$$

$$\begin{aligned}
\hat{t}_{12\uparrow}\phi_5 &= \hat{C}^{\dagger}_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}(-\hat{C}^{\dagger}_{2\uparrow}\hat{C}_{1\uparrow})\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= -\hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{2\downarrow}(\hat{C}_{1\uparrow}|\rangle) \\
&= |\rangle
\end{aligned}$$

and

$$\begin{aligned}
\hat{t}_{12\uparrow}\phi_6 &= \hat{C}^{\dagger}_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^{\dagger}_{1\downarrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}(-\hat{C}^{\dagger}_{1\downarrow}\hat{C}_{1\uparrow})\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= -\hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{1\downarrow}\hat{C}_{1\uparrow}\hat{C}^{\dagger}_{2\downarrow}|\rangle \\
&= \hat{C}^{\dagger}_{2\uparrow}\hat{C}^{\dagger}_{1\downarrow}\hat{C}^{\dagger}_{2\downarrow}(\hat{C}_{1\uparrow}|\rangle) \\
&= |\rangle.
\end{aligned}$$

In summary, one gets for all $\hat{t}_{ij\sigma}$ the results showed in Tables B.1 and B.2. For each table, the first column contains the basis elements denoted by ϕ_i. The last two columns show the action of $\hat{t}_{12\uparrow}$ and $\hat{t}_{21\uparrow}$ on ϕ_i and $\hat{t}_{12\downarrow}$ and $\hat{t}_{21\downarrow}$ on ϕ_i for Tables B.1 and B.2 respectively. From the second row, each column contains, apart the second quantization representation of the wave function or its images, the corresponding graphic representation of the spin configuration. The upwards arrow stands for spin up electron while the downwards arrow stands for spin down electron. The two sites are figured by the two ellipses where the first and the second stands for the first and the second site respectively.
Accordingly to these tables, one observes that the kinetic operator really conveys the idea of moving an electron from one site to the nearest neighbour sites and this characterized the motion of a valence

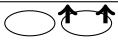
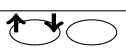
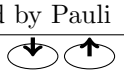
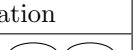
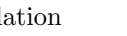
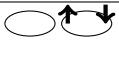
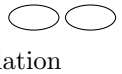
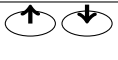
ϕ_i	$\hat{t}_{12\uparrow}\phi_i$	$\hat{t}_{21\uparrow}\phi_i$
$\phi_1 = \hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}\|\rangle$:= 	$\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\uparrow}\|\rangle = \|\rangle$:=  This state is excluded by Pauli	$-\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\|\rangle = \|\rangle$:=  This state is excluded by Pauli
$\phi_2 = \hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\|\rangle$:= 	$\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}\|\rangle = \phi_4$:= 	$\|\rangle$:=  Complete annihilation
$\phi_3 = \hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle$:=	$\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle = \phi_5$:=	$\|\rangle$:=  Complete annihilation
$\phi_4 = \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}\|\rangle$:=	$\|\rangle$:= Complete annihilation	$\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\|\rangle = \phi_2$:= 
$\phi_5 = \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle$:=	$\|\rangle$:=  Complete annihilation	$\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle = \phi_3$:=
$\phi_6 = \hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}\|\rangle$:= 	$\|\rangle$:=  Complete annihilation	$\|\rangle$:=  Complete annihilation

Table B.1: Images $\hat{t}_{ij\sigma}\phi_i$ of the basis elements ϕ_i by $\hat{t}_{12\uparrow}$ and $\hat{t}_{21\uparrow}$.

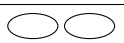
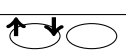
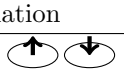
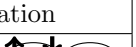
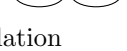
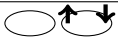
ϕ_i	$\hat{t}_{12\downarrow}\phi_i$	$\hat{t}_{21\downarrow}\phi_i$
$\phi_1 = \hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}\|\rangle$:= 	$\|\rangle$:=  Complete annihilation	$\|\rangle$:=  Complete annihilation
$\phi_2 = \hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\|\rangle$:= 	$\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle = \phi_3$:= 	$\|\rangle$:=  Complete annihilation
$\phi_3 = \hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle$:=	$\|\rangle$:= Complete annihilation	$\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\|\rangle = \phi_2$:= 
$\phi_4 = \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}\|\rangle$:=	$\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle = \phi_5$:= 	$\|\rangle$:= Complete annihilation
$\phi_5 = \hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle$:=	$\|\rangle$:= Complete annihilation	$\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}\|\rangle = \phi_4$:= 
$\phi_6 = \hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}\|\rangle$:= 	$\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\|\rangle = \|\rangle$:=  This state is excluded by Pauli	$-\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{1\downarrow}\|\rangle = \|\rangle$:=  This state is excluded by Pauli

Table B.2: Images $\hat{t}_{ij\sigma}\phi_i$ of the basis elements ϕ_i by $\hat{t}_{12\downarrow}$ and $\hat{t}_{21\downarrow}$.

electron from one atom to another. From the last two tables one can recover the action of the kinetic operator on the basis elements, that reads

$$\begin{aligned}\hat{T}\phi_1 &= -t\Big(\hat{t}_{12\uparrow} + \hat{t}_{21\uparrow} + \hat{t}_{12\downarrow} + \hat{t}_{21\downarrow}\Big)\phi_1 \\ &= 0,\end{aligned}$$

$$\begin{aligned}\hat{T}\phi_2 &= -t\Big(\hat{t}_{12\uparrow} + \hat{t}_{21\uparrow} + \hat{t}_{12\downarrow} + \hat{t}_{21\downarrow}\Big)\phi_2 \\ &= -t\Big(\hat{t}_{12\uparrow} + \hat{t}_{12\downarrow}\Big)\phi_2 \\ &= -t\phi_4 - t\phi_3,\end{aligned}$$

$$\begin{aligned}\hat{T}\phi_3 &= -t\Big(\hat{t}_{12\uparrow} + \hat{t}_{21\uparrow} + \hat{t}_{12\downarrow} + \hat{t}_{21\downarrow}\Big)\phi_3 \\ &= -t\Big(\hat{t}_{12\uparrow} + \hat{t}_{21\downarrow}\Big)\phi_3 \\ &= -t\phi_5 - t\phi_2,\end{aligned}$$

$$\begin{aligned}\hat{T}\phi_4 &= -t\Big(\hat{t}_{12\uparrow} + \hat{t}_{21\uparrow} + \hat{t}_{12\downarrow} + \hat{t}_{21\downarrow}\Big)\phi_4 \\ &= -t\Big(\hat{t}_{21\uparrow} + \hat{t}_{12\downarrow}\Big)\phi_4 \\ &= -t\phi_2 - t\phi_5,\end{aligned}$$

$$\begin{aligned}\hat{T}\phi_5 &= -t\Big(\hat{t}_{12\uparrow} + \hat{t}_{21\uparrow} + \hat{t}_{12\downarrow} + \hat{t}_{21\downarrow}\Big)\phi_5 \\ &= -t\Big(\hat{t}_{21\uparrow} + \hat{t}_{21\downarrow}\Big)\phi_5 \\ &= -t\phi_3 - t\phi_4\end{aligned}$$

and

$$\begin{aligned}\hat{T}\phi_6 &= -t\Big(\hat{t}_{12\uparrow} + \hat{t}_{21\uparrow} + \hat{t}_{12\downarrow} + \hat{t}_{21\downarrow}\Big)\phi_2 \\ &= 0.\end{aligned}$$

Table B.3 highlights the matrix representation of the kinetic operator.

	$\hat{T}\phi_1$	$\hat{T}\phi_2$	$\hat{T}\phi_3$	$\hat{T}\phi_4$	$\hat{T}\phi_5$	$\hat{T}\phi_6$
ϕ_1	0	0	0	0	0	0
ϕ_2	0	0	$-t$	$-t$	0	0
ϕ_3	0	$-t$	0	0	$-t$	0
ϕ_4	0	$-t$	0	0	$-t$	0
ϕ_5	0	0	$-t$	$-t$	0	0
ϕ_6	0	0	0	0	0	0

Table B.3: Images $\hat{T}\phi_i$ of the basis elements ϕ_i by $\hat{T}$.

Now, let us concentrate on some of its properties. It is obvious that

$$\hat{t}^2_{ij\sigma} = 0,$$

and

$$\hat{t}_{ji\sigma}\hat{t}_{ij\sigma} = \hat{\mathbf{1}}$$

regardless the number of sites and electrons. Unfortunately these do not hold for the kinetic operator itself. However, the results of its repeated action on one of $\phi_i, 2 \leq i \leq 5$ show some pattern. Indeed,

for ϕ_2, one gets

$$\begin{aligned}
\hat{T}\phi_2 &= -t\phi_3 - t\phi_4, \\
\hat{T}^2\phi_2 &= -t\hat{T}\phi_3 - t\hat{T}\phi_4, \\
&= (-t)^2\phi_2 + (-t)^2\phi_5 + (-t)^2\phi_2 + (-t)^2\phi_5, \\
&= 2(-t)^2\phi_2 + 2(-t)^2\phi_5, \\
\hat{T}^3\phi_2 &= 2(-t)^2\hat{T}\phi_2 + 2(-t)^2\hat{T}\phi_5, \\
&= 2(-t)^3\phi_3 + 2(-t)^3\phi_4 + 2(-t)^2\phi_2 + 2(-t)^2\phi_4, \\
&= 2^2(-t)^3\phi_3 + 2^2(-t)^3\phi_4, \\
&\vdots \\
\hat{T}^{2n}\phi_2 &= 2^{2n-1}(-t)^{2n}(\phi_2 + \phi_5), \\
\hat{T}^{2n+1}\phi_2 &= 2^{2n}(-t)^{2n+1}(\phi_3 + \phi_4).
\end{aligned}$$

B.1.3 Onsite interaction operator

The onsite interaction operator for two sites and two electrons is read

$$\hat{u} = u_0\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + u_0\hat{n}_{2\uparrow}\hat{n}_{2\downarrow}.$$

While acting on the basis elements, it gives:

$$\begin{aligned}
\hat{u}\phi_1 &= (u_0\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + u_0\hat{n}_{2\uparrow}\hat{n}_{2\downarrow})\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}\hat{C}_{1\downarrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\downarrow}|\rangle \\
&= |\rangle,
\end{aligned}$$

$$\begin{aligned}
\hat{u}\phi_2 &= (u_0\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + u_0\hat{n}_{2\uparrow}\hat{n}_{2\downarrow})\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\
&= -u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{1\uparrow}(\hat{C}_{1\downarrow}\hat{C}^\dagger_{1\downarrow})|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{2\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}(1 - \hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow})|\rangle + |\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}|\rangle + |\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}(1 - \hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\
&= u_0\phi_2,
\end{aligned}$$

$$\begin{aligned}
\hat{u}\phi_3 &= (u_0\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + u_0\hat{n}_{2\uparrow}\hat{n}_{2\downarrow})\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{1\downarrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\uparrow}|\rangle \\
&= |\rangle,
\end{aligned}$$

$$
\begin{aligned}
\hat{u}\phi_4 &= (u_0\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + u_0\hat{n}_{2\uparrow}\hat{n}_{2\downarrow})\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\uparrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{2\downarrow}|\rangle \\
&= |\rangle,
\end{aligned}
$$

$$
\begin{aligned}
\hat{u}\phi_5 &= (u_0\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + u_0\hat{n}_{2\uparrow}\hat{n}_{2\downarrow})\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{1\downarrow}|\rangle - u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}^\dagger_{2\uparrow}(\hat{C}_{2\downarrow}\hat{C}^\dagger_{2\downarrow})|\rangle \\
&= u_0\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\uparrow}(1 - \hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow})|\rangle + |\rangle \\
&= u_0\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle + |\rangle \\
&= u_0\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}(1 - \hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow})|\rangle \\
&= u_0\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= u_0\phi_5,
\end{aligned}
$$

and finally,

$$
\begin{aligned}
\hat{u}\phi_6 &= (u_0\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + u_0\hat{n}_{2\uparrow}\hat{n}_{2\downarrow})\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}|\rangle \\
&= u_0\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{1\downarrow}\hat{C}_{1\downarrow}\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{1\uparrow}|\rangle + u_0\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\downarrow}\hat{C}^\dagger_{1\downarrow}\hat{C}^\dagger_{2\downarrow}\hat{C}_{2\uparrow}|\rangle \\
&= |\rangle.
\end{aligned}
$$

It appears that though $\phi_3 :=$  and $\phi_4 :=$  carry two electrons with opposite spin, these electrons are not interacting whereas they interact for $\phi_2 :=$  and $\phi_5 :=$  . Their difference stems from the site occupation number involved in the definition of the interaction operator. If the Hubbard model we are handling allows neighboring sites to interact, therefore ϕ_3 and ϕ_4 would contribute to the interaction energy. Let us gather the results for $\hat{u}$ into Table B.4. All the

	$\hat{u}\phi_1$	$\hat{u}\phi_2$	$\hat{u}\phi_3$	$\hat{u}\phi_4$	$\hat{u}\phi_5$	$\hat{u}\phi_6$
ϕ_1	0	0	0	0	0	0
ϕ_2	0	u_0	0	0	0	0
ϕ_3	0	0	0	0	0	0
ϕ_4	0	0	0	0	0	0
ϕ_5	0	0	0	0	u_0	0
ϕ_6	0	0	0	0	0	0

Table B.4: Images $\hat{u}\phi_i$ of the basis elements ϕ_i by $\hat{u}$.

basis elements are eigenstates of the interaction operator.

B.1.4 External potential operator

Electrons of the lattice experience the external potential described by $\hat{v} = v_1(\hat{n}_{1\uparrow}+\hat{n}_{1\downarrow})+v_2(\hat{n}_{2\uparrow}+\hat{n}_{2\downarrow})$. Their presence at a site contributes then to the overall energy of the system. For instance

$$\begin{aligned}
\hat{v}\phi_1 &= \Big[v_1(\hat{n}_{1\uparrow}+\hat{n}_{1\downarrow})+v_2(\hat{n}_{2\uparrow}+\hat{n}_{2\downarrow})\Big]\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= v_1\hat{n}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle + v_2\hat{n}_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= v_1\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle + v_2\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= v_1\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}\hat{C}_{1\uparrow}\hat{C}^\dagger_{1\uparrow}|\rangle - v_2\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\uparrow}\hat{C}_{2\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= v_1\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}(1-\hat{C}^\dagger_{1\uparrow}\hat{C}_{1\uparrow})|\rangle - v_2\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\uparrow}(1-\hat{C}^\dagger_{2\uparrow}\hat{C}_{2\uparrow})|\rangle \\
&= v_1\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle - v_2\hat{C}^\dagger_{2\uparrow}\hat{C}^\dagger_{1\uparrow}|\rangle \\
&= v_1\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle + v_2\hat{C}^\dagger_{1\uparrow}\hat{C}^\dagger_{2\uparrow}|\rangle \\
&= (v_1+v_2)\phi_1.
\end{aligned}$$

The following table resumes the images of the basis elements by $\hat{v}$.

	$\hat{u}\phi_1$	$\hat{u}\phi_2$	$\hat{u}\phi_3$	$\hat{u}\phi_4$	$\hat{u}\phi_5$	$\hat{u}\phi_6$
ϕ_1	v_1+v_2	0	0	0	0	0
ϕ_2	0	$2v_1$	0	o	0	0
ϕ_3	0	0	v_1+v_2	0	0	0
ϕ_4	0	0	0	v_1+v_2	0	0
ϕ_5	0	0	0	0	$2v_2$	0
ϕ_6	0	0	0	0	0	v_1+v_2

Table B.5: Images $\hat{v}\phi_i$ of the basis elements ϕ_i by $\hat{v}$.

B.1.5 Exact diagonalization of the Hubbard Hamiltonian

The action of the Hubbard Hamiltonian on the finite dimension Hilbert space $\mathcal{H}_-^{\otimes n_e}$ basis generates the Hubbard Hamiltonian matrix. According to TablesB.3, B.4 and B.5, the Hamiltonian matrix is

$$H = \begin{pmatrix}
v_1+v_2 & 0 & 0 & 0 & 0 & 0 \\
0 & u_0+2v_1 & -t & -t & 0 & 0 \\
0 & -t & v_1+v_2 & 0 & -t & 0 \\
0 & -t & 0 & v_1+v_2 & -t & 0 \\
0 & 0 & -t & -t & u_0+2v_2 & 0 \\
0 & 0 & 0 & 0 & 0 & v_1+v_2
\end{pmatrix}. \tag{B.1}$$

The Shrödinger equation based on the Hubbard Hamiltonian matrix is an eigenvalue problem. An effective way of solving such problem is by performing an exact diagonalization. The prefix exact misleads the understanding by conveying the idea of exact solution. Indeed, except for small dimension Hilbert space, that is small particle number ($n_e \leq 4$), the eigenvalue problems is really tricky to be

solved exactly. Therefore numerical approximations draw upon methods like the Lanczos algorithm [88] or the Bethe ansatz [37] are used instead. Since these numerical approximations are highly accurate, the method is called exact. For this thesis we use octave for numerical resolution of equations. For practical example, let us consider $t = 1, u_0 = -2$ and $v_{i\sigma} = 1$. The Hamiltonian reads

$$H = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 0 & 0 \\ 0 & -1 & 2 & 0 & -1 & 0 \\ 0 & -1 & 0 & 2 & -1 & 0 \\ 0 & 0 & -1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2 \end{pmatrix} \tag{B.2}$$

and has

$$\begin{aligned} \Psi_0 &= 0.602\phi_2 + 0.372\phi_3 + 0.372\phi_4 + 0.602\phi_5, \\ \Psi_1 &= -0.707\phi_2 + 0.707\phi_5, \\ \Psi_2 &= 0.707\phi_3 - 0.707\phi_4, \\ \Psi_3 &= \phi_1, \\ \Psi_4 &= \phi_6, \end{aligned}$$

and

$$\Psi_5 = 0.372\phi_2 - 0.602\phi_3 - 0.602\phi_4 + 0.372\phi_5$$

for wave functions with Ψ_0 the ground state wave function.

B.2 Two sites with one electron

The exercise for one electron necessities a general method regardless the number of site. So, we consider L site lattice with one electron. While acting on the wave function

$$\varphi = \sum_{i=1}^{L} g(x_i) \, |x_i\rangle$$

by the Hubbard Hamiltonian $\hat{H}$, one reaches

$$\hat{H}\varphi = -t \sum_{i=1}^{L} \sum_{s=\pm 1} g(x_i) \, |x_{i+s}\rangle + \sum_{i=1}^{L} v_i g(x_i) \, |x_i\rangle \quad = -t \sum_{i=1}^{L} \left(\sum_{s=\pm 1} g(x_{i+s}) \right) |x_i\rangle + \sum_{i=1}^{L} v_i g(x_i) \, |x_i\rangle \, .$$

Then,

$$\begin{aligned} \hat{H}\varphi = \epsilon\varphi \iff -t \left(\sum_{s=\pm 1} g(x_{i+s}) \right) + v_i g(x_i) \quad &= \quad \epsilon g(x_i) \\ \iff \Big(-t\delta_{(i-1)j} + v_i \delta_{ij} - t\delta_{(i+1)j} \Big)_{ij} \Big(g(x_j) \Big)_{j1} \quad &= \quad \epsilon \Big(g(x_i) \Big)_{i1}. \end{aligned}$$

The matrix $\Big(-t\delta_{(i-1)j} + v_i\delta_{ij} - t\delta_{(i+1)j}\Big)_{ij}$ is an hermitian L squared matrix. Thus, it admits L eigenvalues ϵ_i. This confirms that the ground state wave function for a one particle lattice system is on the form of φ. Furthermore,

$$\begin{aligned}\hat{H}\varphi = \epsilon\varphi &\Longleftrightarrow \left(\sum_{s=\pm 1} g(x_{i+s})\right) = \frac{v_i - \epsilon}{t} g(x_i) \\ &\Longleftrightarrow \left(\sum_{s=\pm 1} g(x_{i+s})\right) = a_i g(x_i),\end{aligned}$$

where

$$a_i = \frac{v_i - \epsilon}{t}.$$

Therefore, for $L = 2$, it follows that

$$\begin{aligned}\hat{H}\varphi = \epsilon\varphi \qquad &\Longleftrightarrow \qquad \begin{cases} g(x_2) &= a_1 g(x_1) \\ g(x_1) &= a_2 g(x_2) \end{cases} \\ &\Longleftrightarrow \qquad a_1 a_2 = 1 \\ &\Longleftrightarrow \qquad \epsilon^2 - (v_1 + v_2)\epsilon + v_1 v_2 - t^2 = 0 \\ &\Longleftrightarrow \qquad \epsilon = \frac{v_1 + v_2 \pm \sqrt{(v_1 - v_2)^2 + 4t^2}}{2}.\end{aligned}$$

Appendix C

Jastrow Factors

In this appendix we derive an expressions for the Jastrow factors γ_{x^m}. In the first section we derive an expression that couples all the Jastrow factors and this can be used to self-consistently determine the Jastrow factors for a fixed single particle ground state wave function and a many particle ground state energy. In the second section we derive expressions for the derivative of the Jastrow factors as a function of site potentials.

C.1 Self consistent expression for Jastrow factors

Recall that we can expand the interacting, $|\Psi\rangle$, and noninteracting, $|\Phi\rangle$, ground state wave functions in terms of a set of basis functions $|\phi_m\rangle$:

$$|\Psi\rangle = \sum_{\Xi_0} f_m |\phi_m\rangle \tag{C.1}$$

and

$$|\Phi\rangle = \sum_{\Xi_0} g_m |\phi_m\rangle . \tag{C.2}$$

The basis functions are Slater determinants

$$|\phi_m\rangle = |\phi_m\rangle = \hat{C}^\dagger_{m_1\uparrow}\hat{C}^\dagger_{m_2\uparrow}\cdots\hat{C}^\dagger_{m_{N_\uparrow}\uparrow}\hat{C}^\dagger_{m_{N_\uparrow+1}\downarrow}\hat{C}^\dagger_{m_{N_\uparrow+2}\downarrow}\cdots\hat{C}^\dagger_{m_{N_\uparrow+N_\downarrow}}|\rangle,$$

and can be represented in terms of the n_e-tuples

$$x^m = (x^m_1, x^m_2, \cdots, x^m_{n_e}). \tag{C.3}$$

f_m and g_m are all non-zero and have the same sign. For a n_e-electron system, we defined the 'Jastrow' operator as

$$\hat{J} = e^{-\sum_o \gamma_o \hat{x}^o},$$

where

$$\hat{x}^m = \hat{x}^m_1 \cdots \hat{x}^m_{n_e}. \tag{C.4}$$

Here $\hat{x}_i$ is equal to $\hat{n}_{x_i\uparrow}$ if $i \leq N_\uparrow$ or $\hat{n}_{x_i\downarrow}$ otherwise. It follows that

$$\hat{x}^m |\phi_n\rangle = \delta_{nm}|\phi_n\rangle; \tag{C.5}$$

therefore, the Jastrow operator maps $|\Phi\rangle$ unto $|\Psi\rangle$

$$\begin{aligned} |\Psi\rangle &= \hat{J}\,|\Phi\rangle \\ &= \sum_m e^{-\gamma_m} g(x^m)|x^m\rangle. \end{aligned} \tag{C.6}$$

The basis functions are eigenfunctions of the Jastrow operator: Acting on a basis function $|x^m\rangle$ with $\hat{J}$ yields

$$\hat{J}|x^m\rangle = e^{-\gamma_{x^m}}|x^m\rangle. \tag{C.7}$$

We can expand the independent particle ground state as

$$|\Phi\left[v^s\right]\rangle = \sum_m g(x^m)\,|x^m\rangle\,, \tag{C.8}$$

where v^s is a general single particle potential and one has $g[v^s]$. For convenience of notation, we suppress the dependence of g on v^s. We have,

$$\begin{aligned} \hat{J}^{-1}\hat{T}\hat{J}\,|\Phi\left[v_0\right]\rangle &= \sum_m g(x^m)\hat{J}^{-1}\hat{T}\hat{J}\,|x^m\rangle \\ &= \sum_m g(x^m)e^{-\gamma_{x^m}}\,\hat{J}^{-1}\hat{T}|x^m\rangle \\ &= -t\sum_m g(x^m)e^{-\gamma_{x^m}}\,\hat{J}^{-1}\sum_{i=1}^{n_e}\sum_{s=\pm 1}|x_1^m\cdots x_i^m+s\cdots x_{n_e}^m\rangle \\ &= -t\sum_m g(x^m)e^{-\gamma_{x^m}}\sum_{i=1}^{n_e}\sum_{s=\pm 1}e^{\gamma_{x^m}(x_i^m+s)}|x_1^m\cdots x_i^m+s\cdots x_{n_e}^m\rangle, \end{aligned} \tag{C.9}$$

where $x^m\left(x_i^m+s\right)$ stands for the n_e-tuple x^m with the i^{th} entry replaced by x_i+s,

$$x^m\left(x_i^m+s\right) \equiv (x_1^m, x_2^m, \cdots, x_i^m+s, ...x_{n_e}^m).$$

Taking the overlap of Eq. (C.9) with $\langle x^n|$ results in

$$\begin{aligned} \langle x^n|\hat{J}^{-1}\hat{T}\hat{J}\Phi\rangle &= -t\,\langle x^n|\sum_m g(x^m)e^{-\gamma_{x^m}}\sum_{i=1}^{n_e}\sum_{s=\pm 1}e^{\gamma_{x^m}(x_i^m+s)}|x_1^{\ m}\cdots x_i^{\ m}+s\cdots x_{n_e}^m\rangle \\ &= -t\sum_m g(x^m)e^{-\gamma_{x^m}}\sum_{i=1}^{n_e}\sum_{s=\pm 1}e^{\gamma_{x^m}(x_i^m+s)}(x^m(x_i^m+s)\equiv x^n). \end{aligned}$$

Only a few terms survive the summation over m and the expression can be contracted to

$$\langle x^n|\hat{J}^{-1}\hat{T}\hat{J}\Phi\rangle = -t\sum_{i=1}^{n_e}\sum_{s=\pm 1}g(x^n(x_i^n-s))e^{-\gamma_{x^n}(x_i^n-s)}e^{\gamma_{x^n}}. \tag{C.10}$$

The Hubbard Hamiltonian we are working with has the form

$$\hat{H} = \hat{T}+\hat{u}+\hat{v}.$$

Since $|\Psi\rangle = \hat{J}\,|\Phi\rangle$, and $\hat{J}$ commutes with $\hat{u}+\hat{v}$, we have

$$\left(\hat{J}^{-1}\hat{T}\hat{J}+\hat{u}+\hat{v}\right)|\Phi\rangle = E\,|\Phi\rangle\,, \tag{C.11}$$

where E is the ground state eigenenergy of $\hat{H}$. We have from Eq. (C.11), using Eq. (C.10), that

$$\begin{aligned}\langle x^n|\,\hat{J}^{-1}\left[v^s\right]\hat{T}J\left[v^s\right]|\Phi\left[v^s\right]\rangle &= \langle x^n|\,E-(\hat{u}+\hat{v})\,|\Phi\left[v^s\right]\rangle \\ &= -t\sum_{i=1}^{n_e}\sum_{s=\pm1} g(x^n(x_i^n+s))e^{-\gamma_{x^n}(x_i^n+s)}e^{\gamma_{x^n}}. \end{aligned} \tag{C.12}$$

The basis functions $|x^m\rangle$ are eigenfunctions of $\hat{u}+\hat{v}$: $(\hat{u}+\hat{v})\,|x^m\rangle = z\,|x^m\rangle$, where z is a real number. It implies that

$$\langle x^n|\,E-(\hat{u}+\hat{v})\,|\Phi\left[v^s\right]\rangle = g\left(x^n\right)\langle x^n|\,E-(\hat{u}+\hat{v})\,|x^n\rangle\,,$$

which allows us to write

$$e^{\gamma_{x^n}} = \frac{g\left(x^n\right)\langle x^n|\,E-(\hat{u}+\hat{v})\,|x^n\rangle}{-t\sum_{i=1}^{n_e}\sum_{s=\pm1} g(x^n(x_i^n+s))e^{-\gamma_{x^n}(x_i^n+s)}}. \tag{C.13}$$

Before attempting to use this expression, let us examine some of its properties. If we substitute $e^{\gamma_{x^n}}$ by $\lambda e^{\gamma_{x^n}}$ where λ is a constant, we also find a solution to Eq. (C.13). However, we work with normalised wave functions. So,

$$|\Psi\rangle = \sum_n e^{-\gamma_{x^n}} g\left(x^n\right)|x^n\rangle$$

implies

$$\begin{aligned} 1 &= \langle\Psi\,|\Psi\rangle \\ &= \sum_X e^{-2\gamma_{x^n}} g^2\left(x^n\right). \end{aligned}$$

This additional condition facilitates a way to 'normalise' $e^{-\gamma_{x^n}}$. Let $\left\{e^{-\tilde{\gamma}_{x^n}}\right\}$ be a solution of Eq. (C.13). If

$$\sum_X e^{-2\tilde{\gamma}_{x^n}} g^2\left(_{x^n}\right) = \chi,$$

then

$$\sum_X \frac{e^{-2\tilde{\gamma}_{X'}}}{\chi} g^2\left(X\right) = 1$$

and

$$e^{-\gamma_{x^n}} = \sqrt{\frac{e^{-2\tilde{\gamma}_{x^n}}}{\chi}}$$

will satisfy Eq. (C.13) and ensure that $|\Psi\rangle$ is normalised if $|\Phi\rangle$ is normalised.

C.2 Derivative of the Jastrow factors with respect to single particle site potentials

From the definition of $\hat{J}\left[v^s\right]$, the $e^{-\gamma_{x^n}}$ are functionals of v^s. We can formulate an expression for the functional derivative of $e^{-\gamma_{x^n}}$ with respect to the site potentials v_k^s from Eq. (C.13):

$$\begin{aligned}\frac{de^{\gamma_{x^n}}}{dv_k^s} &= \frac{\frac{dg(x^n)}{dv_k^s}\langle x^n|\,E-(\hat{u}+\hat{v})\,|x^n\rangle}{-t\sum_{i=1}^{n_e}\sum_{s=\pm1} g(x^n(x_i^n+s))e^{-\gamma_{x^n}(x_i^n+s)}} \\ &\quad + \frac{g\left(x^n\right)\langle x^n|\,E-(\hat{u}+\hat{v})\,|x^n\rangle\sum_{i=1}^{n_e}\sum_{s=\pm1}\frac{d}{dv_k^s}g\left(x^n(x_i^n+s)\right)e^{-\gamma_{x^n}(x_i^n+s)}}{t\left(\sum_{i=1}^{n_e}\sum_{s=\pm1} g(x^n(x_i^n+s))e^{-\gamma_{x^n}(x_i^n+s)}\right)^2}. \end{aligned}$$

Since

$$\frac{d}{dv_k^s} g\left(x^n(x_i^n+s)\right) e^{-\gamma_{x^n(x_i^n+s)}} = e^{-\gamma_{x^n(x_i^n+s)}} \frac{d}{dv_k^s} g(x^n(x_i^n+s)) + g(x^n(x_i^n+s)) \frac{d}{dv_k^s} e^{-\gamma_{x^n(x_i^n+s)}},$$

we can re-arrange this equation to give

$$\begin{aligned} & t\sum_{i=1}^{n_e}\sum_{s=\pm 1} g(x^n(x_i^n+s)) e^{-\gamma_{x^n(x_i^n+s)}} e^{2\gamma_{x^n}} \frac{de^{-\gamma_{x^n}}}{dv_k^s} \\ & + \frac{g\left(x^n\right)\left\langle x^n\right| E-(\hat{u}+\hat{v})\left|x^n\right\rangle \sum_{i=1}^{n_e}\sum_{s=\pm 1} g\left(x^n(x_i^n+s)\right) \frac{d}{dv_k^s} e^{-\gamma_{x^n(x_i^n+s)}}}{\sum_{i=1}^{n_e}\sum_{s=\pm 1} g(x^n(x_i^n+s)) e^{-\gamma_{x^n(x_i^n+s)}}} \\ = & \frac{dg\left(x^n\right)}{dv_k^s}\left\langle x^n\right| E-(\hat{u}+\hat{v})\left|x^n\right\rangle \\ & - \frac{g\left(x^n\right)\left\langle x^n\right| E-(\hat{u}+\hat{v})\left|x^n\right\rangle \sum_{i=1}^{n_e}\sum_{s=\pm 1} e^{-\gamma_{x^n(x_i^n+s)}} \frac{d}{dv_k^s} g\left(x^n(x_i^n+s)\right)}{\sum_{i=1}^{n_e}\sum_{s=\pm 1} g(x^n(x_i^n+s)) e^{-\gamma_{x^n(x_i^n+s)}}}. \end{aligned} \tag{C.14}$$

This can be written as a set of linear equations for $\frac{de^{-\gamma_{x^n}}}{dv_k^s}$:

$$\sum_m A_{nm}\left(v^s\right) \frac{de^{-\gamma_{x^m}}}{dv_k^s} = B_n\left(v_k^s\right),$$

where

$$\begin{aligned} B_n\left(v_k^s\right) = & \frac{dg\left(x^n\right)}{dv_k^s}\left\langle x^n\right| E-(\hat{u}+\hat{v})\left|x^n\right\rangle \\ & - \frac{g\left(x^n\right)\left\langle x^n\right| E-(\hat{u}+\hat{v})\left|x^n\right\rangle \sum_{i=1}^{n_e}\sum_{s=\pm 1} e^{-\gamma_{x^n(x_i^n+s)}} \frac{d}{dv_k^s} g\left(x^n(x_i^n+s)\right)}{\sum_{i=1}^{n_e}\sum_{s=\pm 1} g(x^n(x_i^n+s)) e^{-\gamma_{x^n(x_i^n+s)}}}, \end{aligned}$$

and

$$\begin{aligned} A_{nm}\left(v^s\right) = & t\sum_{i=1}^{n_e}\sum_{s=\pm 1} g(x^n(x_i^n+s)) e^{-\gamma_{x^n(x_i^n+s)}} e^{2\gamma_{x^n}} \delta_{nm} \\ & + \frac{g\left(x^n\right)\left\langle x^n\right| E-(\hat{u}+\hat{v})\left|x^n\right\rangle \sum_{i=1}^{n_e}\sum_{s=\pm 1} g\left(x^n(x_i^n+s)\right)}{\sum_{i=1}^{n_e}\sum_{s=\pm 1} g(x^n(x_i^n+s)) e^{-\gamma_{x^n(x_i^n+s)}}} \delta_{\{x^n\}\left\{x^m(x_i^m-s)\right\}}. \end{aligned}$$

$\delta_{\{x^n\}\left\{x^m(x_i^m-s)\right\}}$ is non-zero, equal to one, only if the n_e-tuples x^n and x^m satisfy

$$(x_1^n, x_2^n, \cdots, x_{n_e}^n) \equiv (x_1^m, x_2^m, \cdots x_i^m - s, ..., x_{n_e}^m).$$

For a given v^s, the matrix $A\left(v^s\right)$ and vector $B\left(v_k^s\right)$ can be determined and then

$$\frac{de^{-\gamma}}{dv_k^s} = A^{-1}\left(v^s\right) B\left(v_k^s\right).$$

$A^{-1}\left(v^s\right)$ is common, but $B\left(v_k^s\right)$ has to be calculated for each site k.

Appendix D

Optimised Perturbation Theory

In this appendix we discuss 1) a scheme for calculating the derivative of the expansion coefficients of the independent particle ground state wave function and 2) a scheme for evaluating the inverse of $\frac{d\rho_k}{dv_i}$, the matrix of the derivatives of the site densities ρ_k with respect to the site potentials v_i .

We expand the ground state wave function as

$$|\Phi\rangle = \sum_m g\left(x^m\right)|x^m\rangle$$

where

$$\hat{H}|\Phi\rangle = E|\Phi\rangle$$

and

$$\hat{H} = -t\sum_{\langle k<j\rangle,\sigma}\left(c^\dagger_{k\sigma}c_{j\sigma} + c^\dagger_{j\sigma}c_{k\sigma}\right) + \sum_{j\sigma} v_j c^\dagger_{j\sigma}c_{j\sigma} \tag{D.1}$$

is a single particle Hamiltonian.

Derivatives. The site density can be written as

$$\begin{aligned}\rho_k &= \langle\Phi|\,\hat{n}_{k\uparrow} + \hat{n}_{k\downarrow}\,|\Phi\rangle \\ &= \sum_{mm'} g\left(x^m\right) g\left(x^{m'}\right)\langle x^m|\,\hat{n}_{k\uparrow} + \hat{n}_{k\downarrow}\left|x^{m'}\right\rangle\end{aligned} \tag{D.2}$$

where

$$\hat{n} = c^\dagger_k c_k.$$

We have

$$c^\dagger_{k\uparrow}c_{k\uparrow}|x^m\rangle = \delta_{k\in\left\{x^m_1,\cdots,x^m_{N_\uparrow}\right\}}|x^m\rangle$$

and

$$c^\dagger_{k\downarrow}c_{k\downarrow}|x^m\rangle = \delta_{k\in\left\{x^m_{N_\uparrow+1},\cdots,x^m_{n_e}\right\}}|x^m\rangle$$

from which it follows that

$$\rho_k = \sum_m \left|g\left(x^m\right)\right|^2\left(\delta_{k\in\left\{x^m_1,\cdots,x^m_{N_\uparrow}\right\}} + \delta_{k\in\left\{x^m_{N_\uparrow+1},\ldots,x^m_{n_e}\right\}}\right) \tag{D.3}$$

and

$$\frac{d\rho_k}{dv_i} = 2\sum_m \frac{dg\left(x^m\right)}{dv_i} g\left(x^m\right)\left(\delta_{k\in\left\{x^m_1,\cdots,x^m_{N_\uparrow}\right\}} + \delta_{k\in\left\{x^m_{N_\uparrow+1},\ldots,x^m_{n_e}\right\}}\right).$$

Taking the derivative of Eq. (D.1) with respect to v_i :

$$\frac{dH^{KS}}{dv_i}\left|\Phi\right\rangle + H^{KS}\left|\frac{d}{dv_i}\Phi\right\rangle = \frac{dE^{KS}}{dv_i}\left|\Phi\right\rangle + E^{KS}\left|\frac{d}{dv_i}\Phi\right\rangle$$

or

$$\left(H^{KS} - E^{KS}\right)\left|\frac{d}{dv_i^{KS}}\Phi\right\rangle = \left(\frac{dE^{KS}}{dv_i^{KS}} - \sum_\sigma c_{i\sigma}^\dagger c_{i\sigma}\right)\left|\Phi\right\rangle. \tag{D.4}$$

Now we can take the scalar product from the left with respect to the excited states $\left|\Phi_n\right\rangle$, $n \neq 0$, or the basis elements, $\left|x^m\right\rangle$.

Let us consider the following definition:

$$\left|\frac{d}{dv_i^{KS}}\Phi\right\rangle = \sum_{n>0}\frac{dg_0^n}{dv_i^{KS}}\left|\Phi_n\right\rangle.$$

It follows that

$$\begin{aligned}\left\langle\Phi_n\right|\left(E_n^{KS} - E^{KS}\right)\left|\frac{d}{dv_i^{KS}}\Phi\right\rangle &= -\left\langle\Phi_n\right|\sum_\sigma c_{i\sigma}^\dagger c_{i\sigma}\left|\Phi\right\rangle \\ \frac{dg_0^n}{dv_i^{KS}} &= -\frac{1}{E_n^{KS} - E^{KS}}\sum_m \#\left(i \in x^m\right) g_n\left(x^m\right) g_0\left(x^m\right).\end{aligned}$$

Here $\#\left(i \in x^m\right)$ is the number of times that i appears in the n_e-tuple x^m. This gives hands on

$$\frac{dg_0\left(x^m\right)}{dv_i^{KS}} = \sum_{n>0}\frac{dg_0^n}{dv_i^{KS}}\left\langle x^m\right|\left.\Phi_n\right\rangle.$$

However, this result strongly relies on non-degenerate ground states; otherwise, the term $E_n^{KS} - E^{KS}$ will induce a division by zero that will automatically stop the calculation.

In case we consider

$$\left|\frac{d}{dv_i^{KS}}\Phi\right\rangle = \sum_m \frac{dg_0(x^m)}{dv_i^{KS}}\left|x^m\right\rangle,$$

then

$$\begin{aligned}\left\langle x^m\right|\left(H^{KS} - E^{KS}\right)\left|\frac{d}{dv_i^{KS}}\Phi\right\rangle &= \left\langle x^m\right|\left(\frac{dE^{KS}}{dv_i^{KS}} - \sum_\sigma c_{i\sigma}^\dagger c_{i\sigma}\right)\left|\Phi\right\rangle \\ \sum_{m'}\frac{dg_0(x^{m'})}{dv_i^{KS}}\left(\left\langle x^m\right|H^{\hat{KS}}\left|x^{m'}\right\rangle - E^{KS}\delta_{mm'}\right) &= g_0(x^m)\left(\frac{dE^{KS}}{dv_i^{KS}} - \#(i \in x^m)\right)\end{aligned}$$

for all m. For M basis functions, $\left|x^m\right\rangle$, we get M equations. Since we require the wave functions to be normalised, we also have

$$\begin{aligned}\sum_m g_0\left(x^m\right) g_0\left(x^m\right) &= 1 \\ \sum_m g_0\left(x^m\right)\frac{dg_0\left(x^m\right)}{dv_i^{KS}} &= 0,\end{aligned}$$

which is the $(M+1)^{th}$ equation that serves to check the solution of the first M equations. With the

M squared and the M column matrices:

$$G = \left[\langle x^m | \, H^{\hat{KS}} \left| x^{m'} \right\rangle - E^{KS} \delta_{mm'} \right]_{1 \leq m,m' \leq M}$$

and

$$B^i \quad = \quad \left[g_0(x^m) \left(\frac{dE^{KS}}{dv_i^{KS}} - \#(i \in x^m) \right) \right]_{1 \leq m \leq M}$$

respectively,

$$\left| \frac{d}{dv_i^{KS}} \Phi \right\rangle = G^{-1} B^i.$$

Note that G does not depend on i.

In this chapter we derive expressions that are suitable for determining the derivative of the expansion coefficients of the ground state wave functions with respect to the independent particle site potentials v_i^0.

D.1 Inverse of $\frac{d\rho_k}{dv_i}$

We cannot easily determine $\frac{dv_k}{d\rho_i}$, but we showed how the response function

$$\frac{d\rho_i}{dv_k} = \frac{d}{dv_k} \langle \Phi | \, \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} \, | \Phi \rangle \, ,$$

can be evaluated in the previous section, from which the inverse matrix $\frac{dv_k}{d\rho_i}$ can be extracted. Note that since a site independent constant shift in the potential does not affect ρ_i, the matrix $\frac{d\rho_i}{dv_k}$ has zero eigenvectors which have to be excluded from the space in which the inverse $\frac{dv_k^{KS}}{d\rho_i}$ is evaluated.

We can express a small change in the site density ρ_i, $\delta\rho_i$, due to small changes in the site potentials δv_k as follows:

$$\delta\rho_i = \sum_k \frac{\delta\rho_i}{\delta v_k} \delta v_k.$$

$\frac{d\rho_i}{dv_k}$is real and symmetric (it is the second derivative of the energy with respect to v_i). It is Hermitian and hence the eigenvalues ε_i of $\frac{\delta\rho_i}{\delta v_k}$,

$$\frac{\delta\rho}{\delta v} \, |\theta_i\rangle = \varepsilon_i \, |\theta_i\rangle$$

are real. The $|\theta_i\rangle$ form a complete basis set. Let $\frac{\delta\rho}{\delta v}$ be the matrix with entries $\frac{\delta\rho_i}{\delta v_k}$ and let $|\delta v\rangle$ be the column vector with entries δv_k. Then,

$$\begin{aligned} |\delta\rho\rangle \quad &= \quad \frac{\delta\rho}{\delta v} \, |\delta v\rangle \\ &= \quad \sum_i \frac{\delta\rho}{\delta v} \, |\theta_i\rangle \, \langle\theta_i| \, \delta v\rangle \\ &= \quad \sum_i \varepsilon_i \, |\theta_i\rangle \, \langle\theta_i| \, \delta v\rangle \, . \end{aligned}$$

Null vectors ($\varepsilon_i = 0$) do not contribute to a change in $\delta\rho_i$ and can be ignored. The vectors $|\theta_i\rangle$ are discrete, $|\theta_i\rangle \equiv \left|\theta_i^1, \theta_i^2, \cdots \theta_i^N\right\rangle$, and allow us to write

$$\frac{1}{\varepsilon_i} \, |\theta_i\rangle \, \langle\theta_i| \, |\delta\rho\rangle = |\theta_i\rangle \, \langle\theta_i| \, \delta v\rangle$$

and

$$\begin{aligned}\sum^{'} \frac{1}{\varepsilon_i} |\theta_i\rangle \langle\theta_i| \, |\delta\rho\rangle &= \left(\sum^{'} |\theta_i\rangle \langle\theta_i|\right) \delta v\rangle \\ &= |\delta\tilde{v}\rangle\end{aligned}$$

where the possible constant potential component has been removed. The prime indicates a summation over the vectors excluding the null vectors. In the space spanned by the eigenvectors of $\frac{\delta\rho}{\delta v}$, excluding the null vectors, $\sum^{'} |\theta_i\rangle \langle\theta_i| \, \delta v\rangle = |\delta v\rangle$ and $\frac{\delta v}{\delta\rho}$ is defined by $\sum^{'} \frac{1}{\varepsilon_i} |\theta_i\rangle \langle\theta_i|$.

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