Density functional theory on a lattice: Self-consistent Hartree plus exchange approximation.

Kossi Amouzouvi and Daniel Joubert

National Institute for Theoretical Physics, School of Physics and Mandelstam Institute for Theoretical Physics, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa.

E-mail: `kossi@aims.edu.gh`

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 show 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 opens the way for solving interesting models such as Hubbard defect chains in a numerically simple and reliable way.

1. 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) [2–4] which is based on the properties of the homogeneous electron gas, 2) Generalized Gradient Approximations (GGA) [5, 6] where the exchange-correlation functional expression includes the gradient of the density, 3) Hybrid functionals [7–9] 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 [10, 11] 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.

2. Background

The simplest Hubbard Hamiltonian [12, 13] for a finite chain single band of length l that contains n_e electrons can be written as

$$\hat{H} = \hat{t} + \hat{u} + \hat{v}. \tag{1}$$

In Eq.(1), $\hat{t} = -t \sum_{\substack{1\leq i,j\leq l \\ j=i\pm1}} \sum_{\sigma=\uparrow,\downarrow} c^{\dagger}_{j\sigma} c_{i\sigma}$, $\hat{u} = u_0 \sum_{1\leq i\leq l} \hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$ 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 wavefunction ψ^0, solution of the Schrödinger equation $\hat{H}\psi^i = E_i\psi^i$, helps to determine the ground state site-density $n_i^0 = \langle\ \psi^0 \mid \sum_{\sigma} \hat{n}_{i\sigma} \mid \psi^0\ \rangle$ and the ground state energy $E_0 = \langle\ \psi^0 \mid \hat{H} \mid \psi^0\ \rangle$. If the ground state energy of a system that exchanges particles with a particle reservoir satisfies the convexity condition [14–16], $E_0(n_e) - E_0(n_e - 1) \leq E_0(n_e + 1) - E_0(n_e)$, it leads to the simple two state ensemble $\Gamma_\alpha[v] = (1-\alpha)\Big|\psi^0[n_e, v]\Big\rangle\Big\langle\psi^0[n_e, v]\Big| + \alpha\Big|\psi^0[n_e + 1, v]\Big\rangle\Big\langle\psi^0[n_e + 1, v]\Big|$ 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 $\langle O\rangle = Tr\Big\{\Gamma_\alpha[v]\hat{O}\Big\}$ 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 non-interacting system with Hamiltonian $\hat{H}_{KS} = \hat{t} + \hat{v}^{KS}$, 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

$$\begin{aligned} E_0(N) &= Tr\left\{\Gamma_\alpha H\right\} \\ &= T_{KS} + E_{HX} + E_C + Tr\left\{\Gamma_\alpha[v^{KS}]\hat{v}\right\} \end{aligned} \tag{2}$$

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 non-interacting Kohn-Sham system. In Eq. (2),

$$\begin{aligned} T_{KS} &= Tr\left\{\Gamma_\alpha\left[v^{KS}\right]\hat{T}\right\}, \\ E_{HX} &= Tr\left\{\Gamma_\alpha\left[v^{KS}\right]\hat{u}\right\}, \\ E_C &= Tr\left\{\Gamma_\alpha\left[v\right]\left(\hat{T} + \hat{u}\right)\right\} - Tr\left\{\Gamma_\alpha\left[v^{KS}\right]\left(\hat{T} + \hat{u}\right)\right\} \end{aligned}$$

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

$$\hat{\tilde{v}}^{KS} = \hat{\tilde{v}}^{HX} + \hat{v}. \tag{3}$$

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.

3. 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 we 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. (3) 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 perturbation theory we compute $\frac{\partial \phi^0}{\partial v^{KS}}$ from which we determine $\frac{\partial n^0}{\partial v^{KS}}$ and $\tilde{v}_0^{HX}$. Finally we obtain a new KS potential v_1^{KS} using Eq. (3). 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 on 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 code written in Octave [17].

4. Results and analysis

The exact KS potential shows a site independent discontinuity at integer particle numbers (Figure 1) if we compare the potential as we approach an integer particle number from below or above. The approximate KS potential (Figure 2) reproduces the shape and the discontinuity observed for the exact potential. In Figure 3 and Figure 4 we notice a shift of the approximate potential with respect to the exact one. The Hartree plus exchange potential has the form

$$v_i^{HX}(N) = (1-\alpha)v_i^{HX}[n_e, v^{KS}(N)] + \alpha v_i^{HX}[n_e + 1, v^{KS}(N)] + E_{HX}(n_e + 1) - E_{HX}(n_e) \tag{4}$$

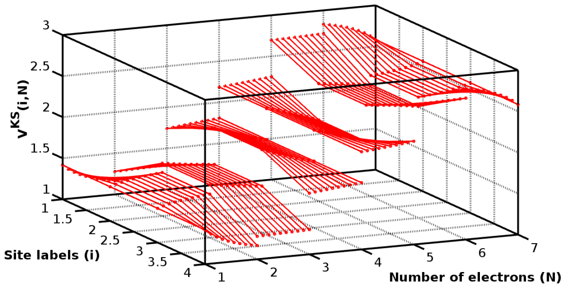

Figure 1. Exact KS potential v^{KS} as a function of particle number for a finite chain.

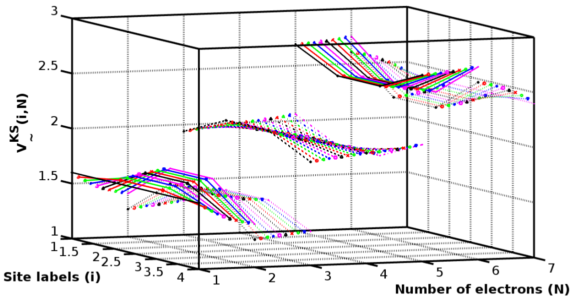

Figure 2. Approximate KS potential $\tilde{v}^{KS}$ as a function of particle number for a finite chain.

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 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.

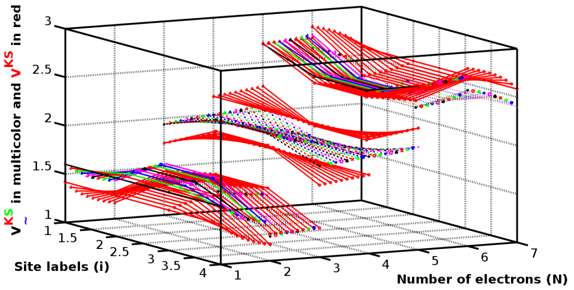

Figure 3. 3D plot of the exact and the approximate KS potentials.

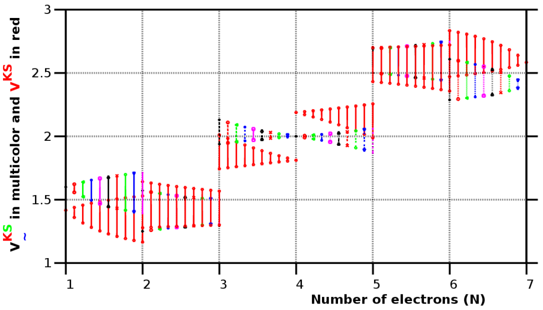

Figure 4. 2D plot of the exact and the approximate KS potentials.

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

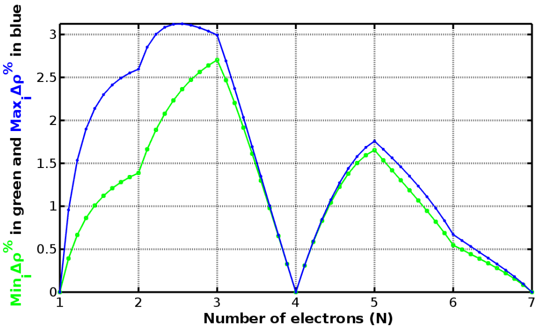

Figure 5. Maximum and minimum density percentage error.

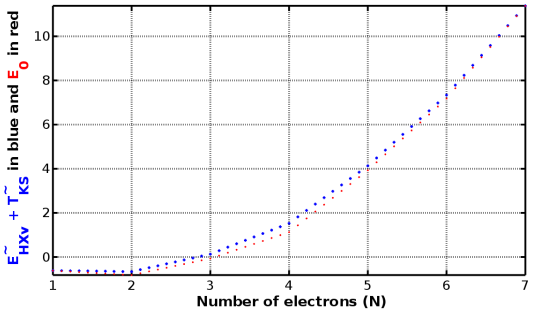

Figure 6. Correlation energy.

5. 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 and discontinuity at integer particle numbers when compared to exact results. The correlation energy, estimated by the difference between the exact and approximate total energies (Figure 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 by using a Jastrow factor to map the KS wave function onto the interacting wave function.

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