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

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. 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. 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 and compare the exact results to a local density approximation to the exchange-correlation functional.

1. Introduction

First introduced by Thomas and Fermi [1] in 1927 and placed on a formally sound base by Hohenberg and Kohn [2] and then formulated in a more practical form by Kohn and Sham [3] in the mid 1960's, Density Functional Theory (DFT) turned out to be a powerful tool for investigating the electronic structure of atoms, molecules or in general a many-electron system. It is mainly used in the material sciences, physics and chemistry. Discussions around DFT formalism, and even doubt about the existence of a well defined exchange-correlation (XC) potential [4] used to explained the problem of calculating the fundamental band gaps [5, 6] encountered in insulator and semiconductor materials, is ongoing. The exact DFT functionals are not known and in practice approximations have to be made to implement DFT. For models where the interacting many particle Hamiltonian can be solved exactly, an exact numerical solution for the fictitious single particle Kohn-Sham DFT equations can be determined and formal properties of DFT can then be investigated. Assessing the formalism and gaining insight into the properties of DFT can be assisted by investigating solvable models. Lattice-DFT [7, 8] is probably one of the best models where DFT theories can be accurately assessed. The simplest of these is the one-dimensional Hubbard model [9−11]. Although it is not possible to find a general analytic solution, there exist analytic solutions for special cases. For small systems Exact Diagonalization of the Hubbard model is feasible and that is the approach we chose. 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 in the exchange-correlation potential as a function of fractional particle numbers in an ensemble formalism.

We focus, in Section 2, on the fundamentals of Lattice-DFT. In Section 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. A thorough summary is included in Section 5.

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 [12]. 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 [13, 14], is satisfied, the energy for fractional particle numbers $J = (1-\alpha)N_e + \alpha(Ne+1)$ 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,

$$\mu = \frac{\delta E(J)}{\delta N_e} \tag{1}$$

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 $J \leq N_e$, $\mu = E(N_e+1) - E(N_e) = A$ or $\mu = E(N_e) - E(N_e-1) = I$, 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:

$$\hat{H} = \sum_{1\leq i,j\leq N,\sigma} t_{ij} C^{\dagger}_{j\sigma} C_{i\sigma} + \sum_{1\leq i\leq N} u_i n_{i\uparrow} n_{i\downarrow} + \sum_{1\leq i\leq N,\sigma} v_{i\sigma} n_{i\sigma}. \tag{2}$$

Here σ is the electron spin and $C^{\dagger}_{i\sigma}$ and $C_{i\sigma}$ 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 $C^{\dagger}_{i\sigma}C_{i\sigma}$. The hopping matrix $\left(t_{ij} = \langle\, \phi_j \mid -\frac{\hbar^2}{2m}\nabla^2 \mid \phi_i \,\rangle\right)_{1\leq i,j\leq N}$ [15] conveys the same idea of motion of particles in a general system. For simplicity, we limited the hopping amplitude up to the first neighbor 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

$$\hat{H} = -t\sum_{\sigma}\left[C^{\dagger}_{2\sigma}C_{1\sigma} + \sum_{i=2}^{N-1}\left(C^{\dagger}_{(i-1)\sigma}C_{i\sigma} + C^{\dagger}_{(i+1)\sigma}C_{i\sigma}\right) + C^{\dagger}_{(N-1)\sigma}C_{N\sigma}\right] + u\sum_{1\leq i\leq N} n_{i\uparrow}n_{i\downarrow} + \sum_{1\leq i\leq N,\sigma} v_i n_{i\sigma}. \tag{3}$$

we solved the finite chain Hubbard Model using Exact Diagonalization (ED). 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 non interacting, or KS system, is addressed in the Hubbard model by setting the on-site coulomb potential to zero and replacing the on-site potential v_i, by the KS potential $v_{ks,i}$.

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 [13]. This condition determines the KS-potential uniquely.

For comparison, we follow reference [16] and define a local density approximation (LDA) for an infinite homogeneous lattice system: the site ground state; Hartree and kinetic energies are approximated by

$$e(t,u,n_i) = \begin{cases} \frac{-2t\beta(t,u)}{\pi} \sin\left(\frac{\pi}{\beta(t,u)} n_i\right) & \text{if } n_i \leq 1 \\ \frac{-2t\beta(t,u)}{\pi} \sin\left(\frac{\pi}{\beta(t,u)}(2-n_i)\right) + u(n_i-1) & \text{otherwise ,} \end{cases} \tag{4}$$

$$e_H = \frac{u}{4} n_i^2 \qquad \text{and} \qquad e_T = e(t,0,n_i). \tag{5}$$

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. Results and analysis

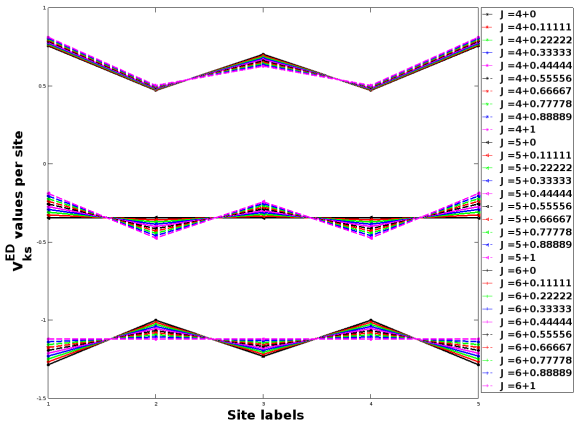

Figure 1. Exact KS potential as a function of particle number for particles in an infinite square well.

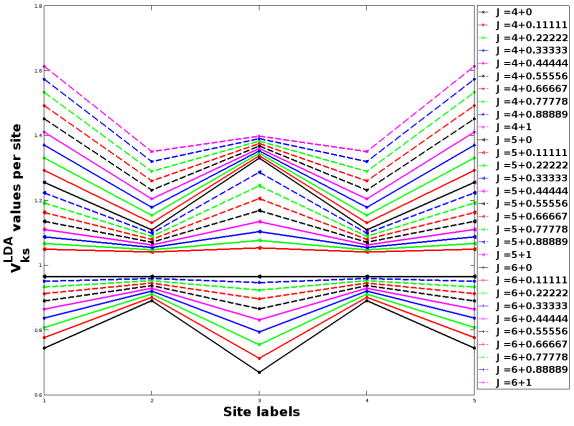

Figure 2. KS potential in the LDA approximation as a function of particle number for particles in an infinity square well.

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 1 results for the exact KS potential are shown as a function of particle number. Figure 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 3. The LDA potential is continuous as a function of particle number as shown in Figure. 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) 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), but the numerical values are quite different.

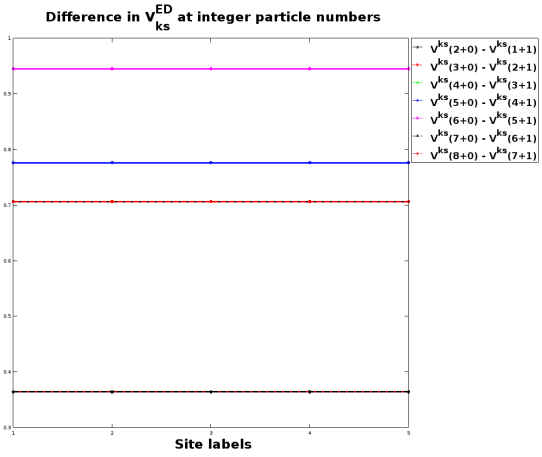

Figure 3. Difference in the exact KS potentials at integer particle numbers for J approaching an integer from above and below.

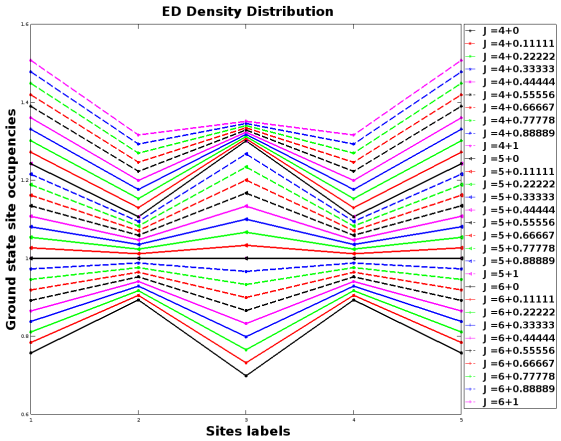

Figure 4. Variation of the ground state density.

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 [13]. As a further study we intend to explore an ensemble definition of the exchange-correlation energy to construct approximations to the KS potential that includes a discontinuity at integer particle numbers.

References

[1] Thomas L H 1927 *Mathematical Proceedings of the Cambridge Philosophical Society* vol 23 (Cambridge Univ Press) pp 542–548
[2] Hohenberg P and Kohn W 1964 *Physical review* **136** B864
[3] Kohn W and Sham L J 1965 *Physical Review* **140** A1133
[4] Zahariev F E and Wang Y A 2004 *Physical Review A* **70** 042503
[5] Sham L and Schlüter M 1983 *Physical Review Letters* **51** 1888
[6] Brosco V, Ying Z J and Lorenzana J 2013 *Scientific reports* **3**

[7] Schönhammer K, Gunnarsson O and Noack R 1995 *Physical Review B* **52** 2504
[8] Schonhammer K and Gunnarsson O 1987 *Journal of Physics C: Solid State Physics* **20** 3675
[9] Hubbard J 1963 *Proc. R. Soc. (London)* A **276**
[10] Essler F H, Frahm H, Göhmann F, Klümper A and Korepin V E 2005 *The one-dimensional Hubbard model* (Cambridge University Press)
[11] Schindlmayr A and Godby R 1995 *Physical Review B* **51** 10427
[12] Joubert D P 2012 *The Journal of chemical physics* **136** 174113
[13] Perdew J P, Parr R G, Levy M and Balduz Jr J L 1982 *Physical Review Letters* **49** 1691
[14] Sagvolden E and Perdew J P 2008 *Physical Review A* **77** 012517
[15] Jafari S A *Iranian Journal of Physics Research* **8** 113–120
[16] Capelle K, Lima N, Silva M and Oliveira L 2003 *The Fundamentals of Electron Density, Density Matrix and Density Functional Theory in Atoms, Molecules and the Solid State* (Springer) pp 145–168