Density Functional Theory on a Lattice

Kossi Kety - Daniel Joubert

AIMS CAMEROON

July 12, 2018

Outline

Introduction: The Many-Body Problem

- Materials are very important in the development of civilization.
- Many of the most pressing scientific problems humans currently face are due to the limits of the materials that are available and how they are used.
- The study of the structure of the matter is governed by the non-relativistic time-independent Schrödinger Equation.

$$\hat{H}\Psi(\boldsymbol{r},\boldsymbol{R}) = E\Psi(\boldsymbol{r},\boldsymbol{R}) \tag{1}$$

$$\begin{aligned}\hat{H} = &-\sum_{i=1}^{N_n}\frac{1}{2M_i}\nabla^2_{\boldsymbol{R}_i} - \frac{1}{2}\sum_{i=1}^{N_e}\nabla^2_{\boldsymbol{r}_i} + \sum_{i}^{N_n}\sum_{j>i}^{N_n}\frac{Z_i Z_j}{|\boldsymbol{R}_i - \boldsymbol{R}_j|} \\ &-\sum_{i=1}^{N_e}\sum_{j=1}^{N_n}\frac{Z_j}{|\boldsymbol{r}_i - \boldsymbol{R}_j|} + \sum_{i=1}^{N_e}\sum_{j>1}^{N_e}\frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\end{aligned} \tag{2}$$

- Equation (1) with the Hamiltonian (2) is very difficult to solve;
- This problem is actually one of the biggest challenge in condensed matter physics, materials science and quantum chemistry: **the quantum mechanical many-body problem.**

There is two distincts strategies to make progress !

- The first approach is the so called *ab initio* strategies and **Density Functional Theory** is the most widely used,
- Second, the construction of **Model Hamiltonians** such as **The Hubbard Model** is used.

- Today, DFT is the standard method for quantitative electronic structure calculations of solids and molecules but it fails while describing strongly correlated systems.

- However, systems characterized by strong electronic correlation are the center of many applications such as solar cells (TiO_2), batteries, high Temperature super-conductors, etc.

- The Hubbard model is used to describe strongly interacting electrons but does not permit quantitative prediction.

- There are four connections between the two approaches. *In this work, we focus on the fourth !*

Introduction: Objectives

- The use of special formulation of DFT called **Site Occupation Functional Theory** (SOFT) to study a lattice Hamiltonian: the Hubbard Model.

- The aim is to show that DFT in the Kohn Sham formulation works on a lattice for integer particles number and use it to investigate the **fundamental gap** problem in DFT.

Theoretical Frame Work: Background on DFT

- Within the *Born-Oppenheimer* approximation:

Electronic Hamiltonian

$$\hat{H}_e = \hat{T}(\boldsymbol{r}) + \hat{V}_{ee}(\boldsymbol{r}) + \hat{V}_{ext}(\boldsymbol{r}) \tag{3}$$

- First *Hohenberg* and *Kohn* theorem:

The Energy Functional

$$\begin{aligned} E\left[n(\boldsymbol{r})\right] =& \langle \Psi | \hat{H} | \Psi \rangle = \langle \Psi | \hat{T}(\boldsymbol{r}) + \hat{V}_{ee}(\boldsymbol{r}) | \Psi \rangle + \langle \Psi | \hat{V}_{ext}(\boldsymbol{r}) | \Psi \rangle \\ =& F\left[n(\boldsymbol{r})\right] + \int V_{ext}(\boldsymbol{r}) n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \end{aligned}$$

Background on DFT

- Second *Hohenberg* and *Kohn* theorem and the *Levy-Lieb* constrained search formulation:

The Ground State Energy

$$E_0 = \min_{\tilde{n} \to N} \left[F_{LL}\left[\tilde{n}(\boldsymbol{r})\right] + \int V_{ext}(\boldsymbol{r})\tilde{n}(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \right] \tag{4}$$

$$F_{LL}\left[\tilde{n}(\boldsymbol{r})\right] = \min_{\tilde{\Psi} \to \tilde{n}} \langle \tilde{\Psi} | \hat{T} + \hat{V}_{ee} | \tilde{\Psi} \rangle \tag{5}$$

Background on DFT

The Kohn-Sham Scheme

$$F_{LL}\left[\tilde{n}(\boldsymbol{r})\right] = T_S\left[\tilde{n}(\boldsymbol{r})\right] + \frac{1}{2}\iint \frac{\tilde{n}(\boldsymbol{r})\tilde{n}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}' + E_{xc}\left[\tilde{n}(\boldsymbol{r})\right] \tag{6}$$

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\boldsymbol{r})\right]\varphi_i(\boldsymbol{r}) = \varepsilon_i\varphi_i(\boldsymbol{r}) \tag{7}$$

$$V_{eff}(\boldsymbol{r}) = V_{ext}(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}' + \frac{\delta E_{xc}}{\delta\tilde{n}(\boldsymbol{r})}\left[\tilde{n}(\boldsymbol{r})\right](\boldsymbol{r}) \tag{8}$$

$$n(\boldsymbol{r}) = \sum_{i=1}^{N}|\varphi_i(\boldsymbol{r})|^2 \tag{9}$$

$$E_0 = \sum_{i=1}^{N}\varepsilon_i + E_{xc}\left[n(\boldsymbol{r})\right] - \int V_{xc}(\boldsymbol{r})n(\boldsymbol{r})\mathrm{d}\boldsymbol{r} - \frac{1}{2}\int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r} \tag{10}$$

Theoretical Frame Work: The Hubbard Model

$$\hat{H} = -t \sum_{\sigma} \left(\hat{c}^{\dagger}_{1\sigma} \hat{c}_{2\sigma} + \hat{c}^{\dagger}_{2\sigma} \hat{c}_{1\sigma} \right) + U \sum_{i} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{i} v_i \hat{n}_i \quad , \tag{11}$$

$$\hat{n}_i = \hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} \quad ; \quad \hat{n}_{i\sigma} = \hat{c}^{\dagger}_{i\sigma} \hat{c}_{i\sigma} \tag{12}$$

$$\left\{ c^{\dagger}_{i\sigma}, c_{j\sigma'} \right\} = c^{\dagger}_{i\sigma} c_{j\sigma'} + c_{j\sigma'} c^{\dagger}_{i\sigma} = \delta_{ij} \delta_{\sigma\sigma'} \tag{13}$$

$$\left\{ c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} \right\} = \{ c_{i\sigma} c_{j\sigma'} \} = 0 \tag{14}$$

Methodology: Exact Diagonalization

- Define a suitable basis of functions and compute the Hamiltonian matrix in this basis.
- The symmetries of the Hamiltonian is used to reduce the dimension of the Hilbert space.
- For the Hubbard model, the total number operator and the total spin operator $\hat{S}_z = \frac{1}{2}\sum_{i=1}^{N}\left(\hat{c}_{i\uparrow}^{\dagger}\hat{c}_{i\uparrow} - \hat{c}_{i\downarrow}^{\dagger}\hat{c}_{i\downarrow}\right)$ commute with the Hamiltonian. The structure of the Hamiltonian matrix is reduced to a block diagonal form, each block corresponding to a fixed value of S_z can be diagonalized independently.

Methodology: Exact Diagonalization

The Hamiltonian Matrix

$$\hat{H} = \begin{pmatrix} U + 2v_1 & -t & -t & 0 \\ -t & 0 & 0 & -t \\ -t & 0 & 0 & -t \\ 0 & -t & -t & U + 2v_2 \end{pmatrix} \tag{15}$$

The ground state energy is the lowest eigenvalue of the Hamiltonian matrix and the ground state density is the expectation value of the number operator with respect to the ground state wave function.

Methodology: DFT for the Hubbard Model

The Kohn-Sham Hamiltonian

$$\hat{H}^{KS} = -t \sum_{\sigma} \left(\hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + \hat{c}_{2\sigma}^{\dagger} \hat{c}_{1\sigma} \right) + \sum_{i} v_i^{KS} \hat{n}_i \quad ; \tag{16}$$

v_i^{KS} = Kohn-Sham potential

- In lattice DFT, the sites occupations $n = \{n_1, n_2, \cdots n_N\}$ are the controlling variables; N = number of site.

The Total Energy Function(al)

$$E[n] = T_S[n] + E_{HX}[n] + E_C[n] + \sum_{i} v_i n_i. \tag{17}$$

DFT for the Hubbard Model

- The Kohn-Sham kinetic energy $T_S[n]$ and the Hartree-exchange term $E_{HX}[n]$ can be computed explicitly. For the spin unpolarized Hubbard model,

The Kohn-Sham potential

$$v_i^{KS} = v_i + \frac{U}{2} n_i + \frac{\partial E_C}{\partial n_i}. \tag{18}$$

DFT for the Hubbard Model

- In practice, the correlation energy is approximated and an approximation to the ground state density and energy can be calculated.
- For the finite Hubbard model, we can compute the exact ground state density n_k by exact diagonalizing the interacting Hubbard Hamiltonian
- Knowing n_k, we can construct the exact Kohn-Sham potential $v^{KS} = \left\{ v_1^{KS}, v_2^{KS}, \cdots, v_N^{KS} \right\}$ using a self-consistent scheme.

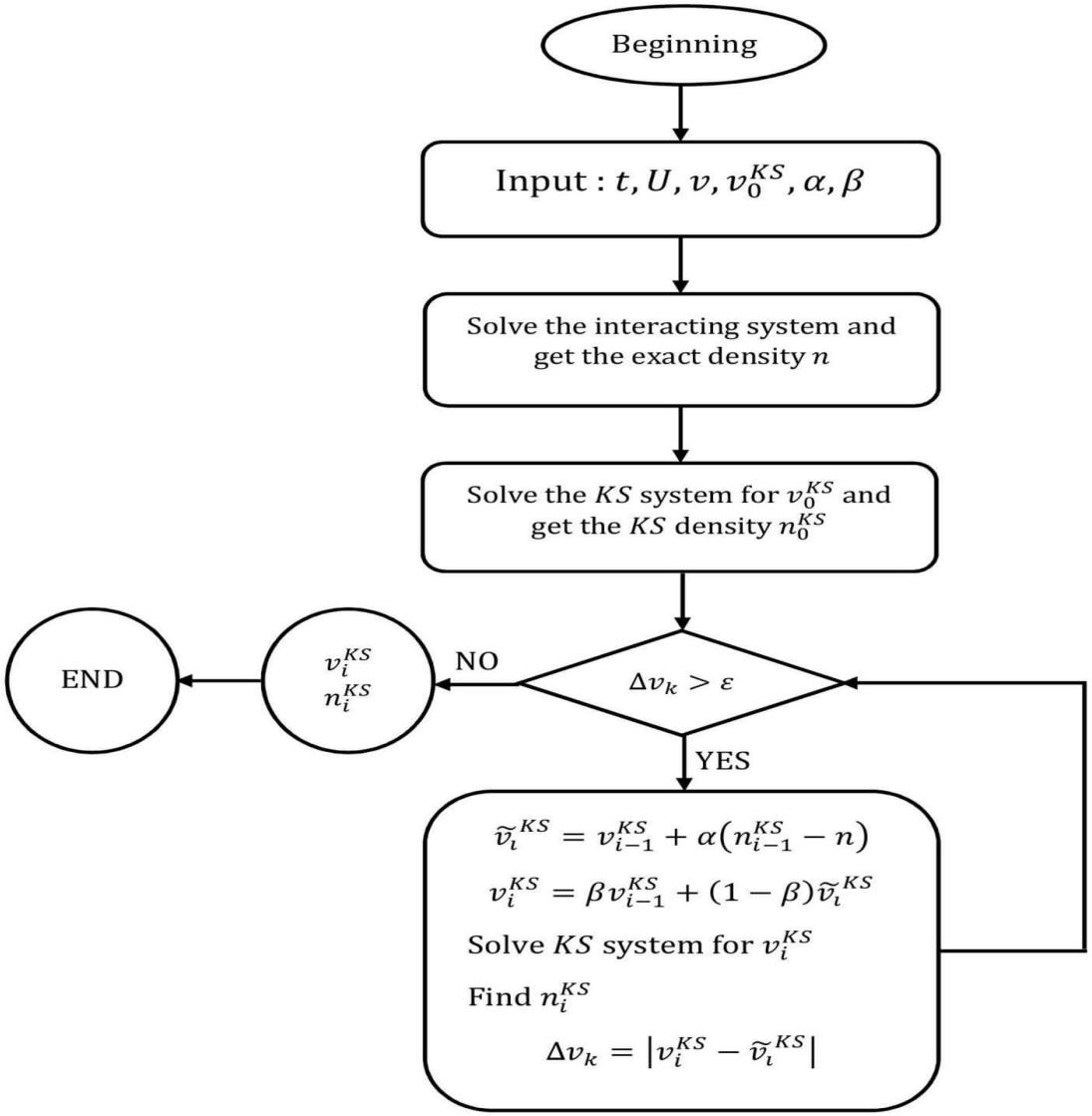

Figure 1: Algorithm for KS scheme .

The Fundamental Gap and the Kohn-Sham Gap

- The fundamental gap of N electrons systems:

$$E_g = I(N) - A(N) \tag{19}$$

- The ionization energy I and the electron affinity denoted A are:

$$I(N) = E(N-1) - E(N) \quad ; \quad A(N) = E(N) - E(N+1). \tag{20}$$

- The Kohn-Sham gap is defined as :

$$E_g^{KS} = \varepsilon^{LUMO} - \varepsilon^{HOMO} \tag{21}$$

The Fundamental Gap and the Kohn-Sham Gap

- According to the Koopman's theorem of DFT:

$$I(N) = -\varepsilon^{HOMO} \tag{22}$$

- The fundamental gap is written as a function of the KS gap:

$$E_g = E_g^{KS} + \Delta xc \quad , \tag{23}$$

Δxc is called the derivative discontinuity contribution to the gap.

- To compute I and A, we solved the Hamiltonian for one and three electrons. We used the Kohn-Sham self consistent scheme to compute the Kohn Sham potential.

Results and Analysis: Ground State Energy

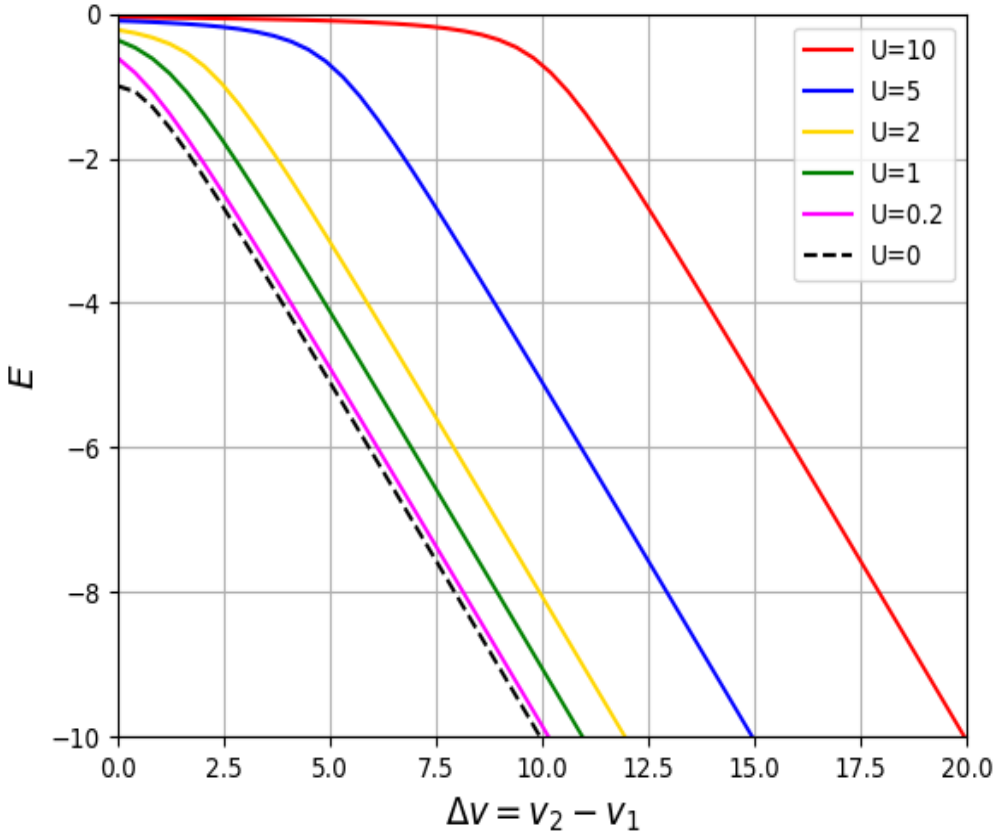

Figure 2: Ground-state energy of Hubbard dimer as a function of Δv for several values of U and $2t = 1$

Results and Analysis: Ground State Density

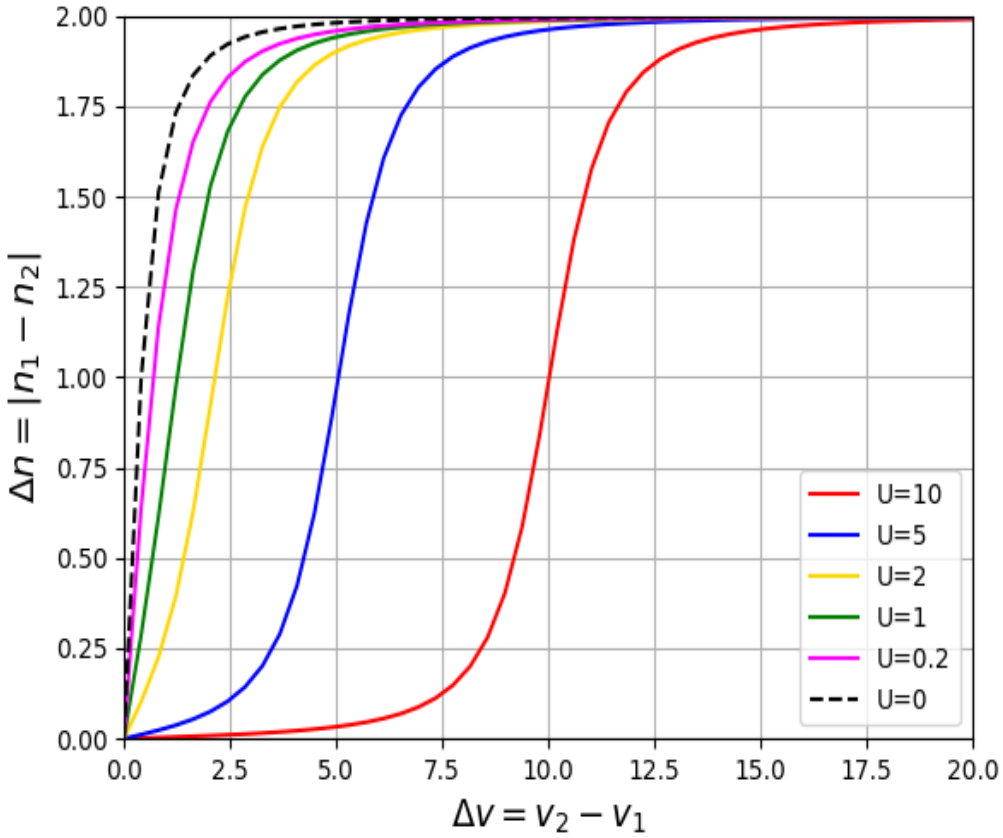

Figure 3: Ground-state occupation of Hubbard dimer as a function of Δv for several values of U and $2t = 1$.

Results and Analysis: The Hubbard Dimer Gap

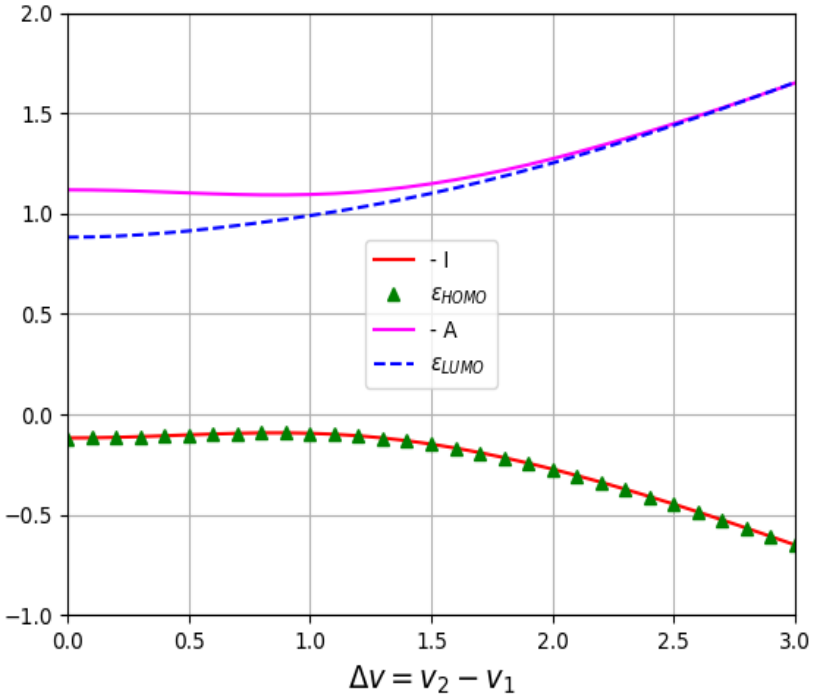

Figure 4: Plot of $-I$, ε^{HOMO}, $-A$ and ε^{LUMO} as a function of Δv with $U = 1$ and $2t = 1$.

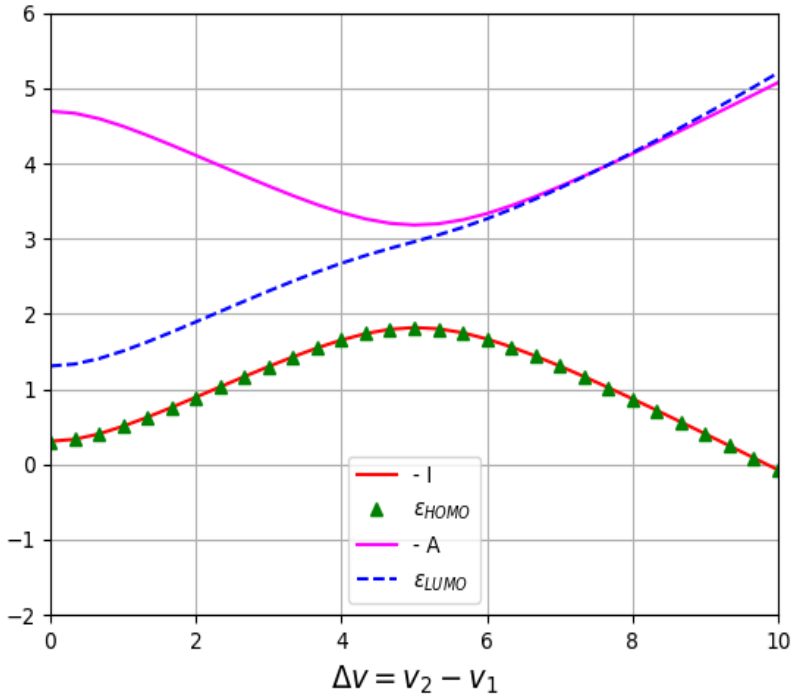

Figure 5: Plot of $-I$, ε^{HOMO}, $-A$ and ε^{LUMO} as a function of Δv with $U = 5$ and $2t = 1$.

Results and Analysis: Derivative Discontinuity

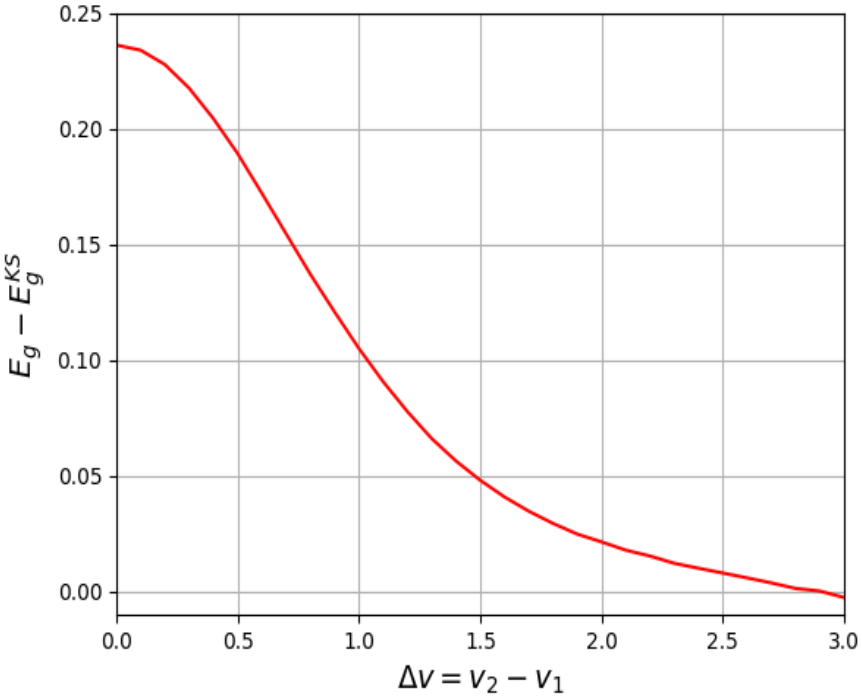

Figure 6: Derivative discontinuity as a function of Δv for $U = 1$ and $2t = 1$.

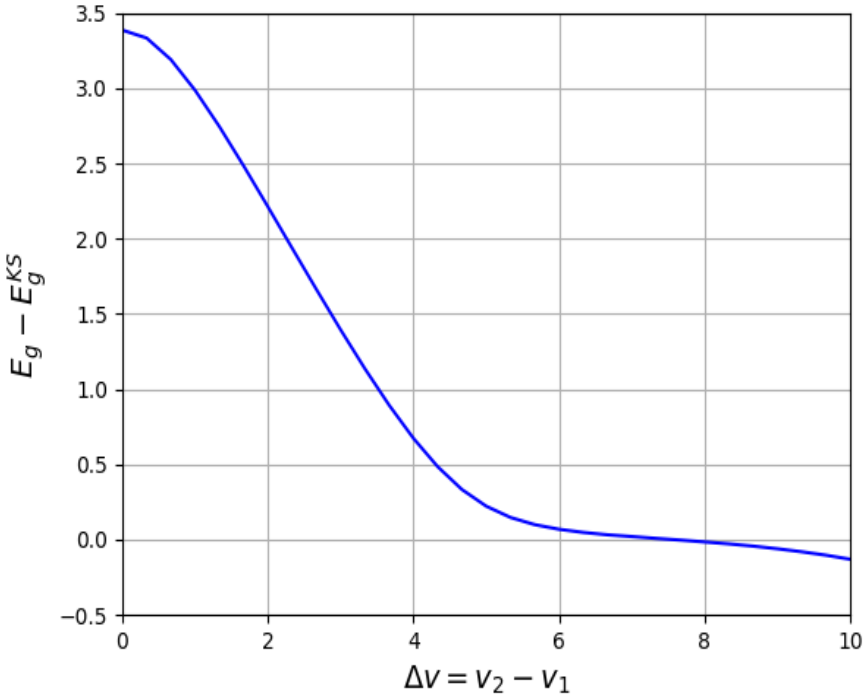

Figure 7: Derivative discontinuity as a function of Δv for $U = 5$ and $2t = 1$.

Result and Analysis

- Most of the time, the KS gap is smaller than the real gap, but for a very asymmetric potential the KS gap can be larger than the real gap.

- Δxc is due to the derivative discontinuity of the exchange correlation potential experienced as the electron number, N, crosses an integer value.

$$\Delta xc = \left.\frac{\delta E_{xc}[n]}{\delta n_i(\boldsymbol{r})}\right|_{N+\delta N} - \left.\frac{\delta E_{xc}[n]}{\delta n_i(\boldsymbol{r})}\right|_{N-\delta N} = V^{(+)}_{xc,i}(\boldsymbol{r}) - V^{(-)}_{xc,i}(\boldsymbol{r}) \quad (24)$$

Results and Analysis

- The band-gap problem of Kohn-Sham density functional theory is current, and many novel approaches have been developed to improve the fundamental gap prediction.

- Δxc Within the Kohn-Sham framework, the optimized effective potential formalism was developed and outside the Kohn-Sham framework, the generalized Kohn-Sham (GKS) theory is used.

Conclusion and Perspectives

- We explore some aspects of DFT using a simple model: The two sites, asymmetric, half-filled Hubbard model.
- We analyzed the ground state energy and density of the Hubbard dimer in function of the on-site potential.
- We showed that DFT works on a lattice for integer particle number by computing self-consistently the Kohn-Sham potential.

Conclusion and Perspectives

- Finally, we have shown that, in the dimer study, the Kohn-Sham gap can be smaller and even larger than the fundamental gap. The Difference is related to the derivative discontinuity of the exchange correlation potential.

- In future work, we expect to find a technique to solve exactly the Kohn-Sham equations and also to perform Time Dependent Lattice DFT to study the excited states of the Hubbard dimer.


THANK YOU
ANY QUESTIONS?