

DFT functional QA

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November 2021

1 Introduction

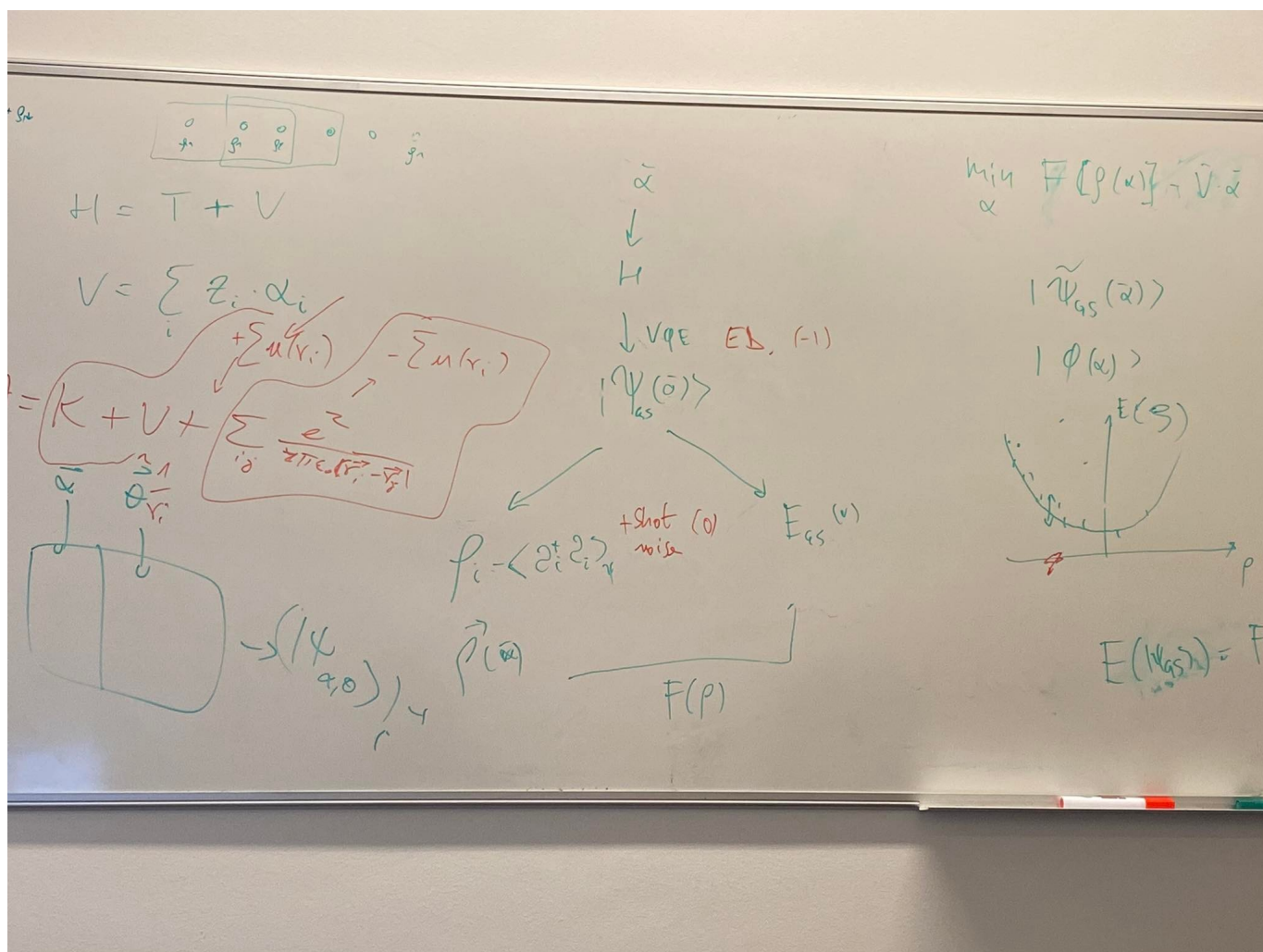


Figure 1: QA image

2 Theory

2.1 Solving the Spinless Hubbard Model

$$\mathbf{H}_{Spinless} = \sum_i^L \epsilon_i \hat{a}_i^\dagger \hat{a}_i - t \sum_{\langle i,j \rangle}^L \hat{a}_i^\dagger \hat{a}_j + U \sum_i^L \hat{n}_i \hat{n}_{i+1}, \quad (1)$$

The model can be solved by writing the Hamiltonian over a convenient representation.

The basis states are the number of possible configurations of the system, composed of L sites and N electrons. For example, for 4 sites and 2 electrons, the wave function of this system can be written as a linear combinations of the basis vectors:

$$\begin{aligned} \mathbf{Basis}_{L=4,N=2} = & (|1\rangle, |2\rangle, |3\rangle, |4\rangle, |5\rangle, |6\rangle) = \\ & (|1, 1, 0, 0\rangle, |1, 0, 1, 0\rangle, |1, 0, 0, 1\rangle, |0, 1, 1, 0\rangle, |0, 0, 1, 1\rangle, |0, 1, 0, 1\rangle). \end{aligned} \quad (2)$$

Each basis state being represented by a vector $|\alpha_1, \alpha_2, \alpha_3, \alpha_4\rangle$, where α_i corresponds to the number of electrons on site i .

The dimension of the Hilbert space of the problem is given by the binomial co-efficient:

$$\binom{L}{N} = \frac{L!}{N!(L-N)!} = n. \quad (3)$$

Once the basis states are generated, the eigenvalues and eigenstates of the problem are computed by representing the Hamiltonian over these states.

2.1.1 Exact Diagonalisation

The matrix elements of the Hamiltonian, i.e. between basis states

$|s\rangle = |\alpha_1^s, \alpha_2^s, \alpha_3^s, \dots, \alpha_{L-1}^s, \alpha_L^s\rangle$ and $|t\rangle = |\alpha_1^t, \alpha_2^t, \alpha_3^t, \dots, \alpha_{L-1}^t, \alpha_L^t\rangle$ are computed via,

$$(H)_{s,t} = \langle s | \mathbf{H}_{Spinless} | t \rangle. \quad (4)$$

The diagonalisation of the matrix $(H)_{s,t}$ will provide the eigenvalues, E_m , (total energies of the system) and their corresponding eigenvectors

$\psi^m = (\beta_1^m, \beta_2^m, \dots, \beta_{n-1}^m, \beta_n^m)$ [5]. The corresponding eigenstate for E_m is the wavefunction,

$$|\psi^m\rangle = \sum_i^n (\beta_i^m |\alpha_1^i, \alpha_2^i, \alpha_3^i \dots \alpha_{L-1}^i, \alpha_L^i\rangle). \quad (5)$$

the Hamiltonian Matrix corresponding to 4 sites at half-filling,

$$H_{L=4,N=2} = \begin{pmatrix} U + \epsilon_1 + \epsilon_2 & -t & 0 & 0 & 0 & -t \\ -t & \epsilon_1 + \epsilon_3 & -t & -t & -t & 0 \\ 0 & -t & U + \epsilon_1 + \epsilon_4 & 0 & 0 & -t \\ 0 & -t & 0 & U + \epsilon_2 + \epsilon_3 & 0 & -t \\ 0 & -t & 0 & 0 & U + \epsilon_3 + \epsilon_4 & -t \\ -t & 0 & -t & -t & -t & \epsilon_2 + \epsilon_4 \end{pmatrix} \quad (6)$$

Red font denotes terms resulting from periodic boundary conditions. For example, the action of $\mathbf{H}_{Spinless}$ on the basis state $|1\rangle = |1, 1, 0, 0\rangle$ for the chain and ring are:

$$\mathbf{H}_{Spinless}|1, 1, 0, 0\rangle = (U + \epsilon_1 + \epsilon_2)|1, 1, 0, 0\rangle - t|1, 0, 1, 0\rangle, \quad (7)$$

$$\mathbf{H}_{Spinless}|1, 1, 0, 0\rangle = (U + \epsilon_1 + \epsilon_2)|1, 1, 0, 0\rangle - t(|1, 0, 1, 0\rangle + |0, 1, 0, 1\rangle). \quad (8)$$

By ED the matrix form of the Schrödinger Equation, $H|\psi\rangle = E|\psi\rangle$, can be solved computationally. Note that matrix diagonalisation is a procedure that requires a computational time scaling as n^3 , where n is the dimension of the matrix to diagonalise. This dimension n , the dimension of the Hilbert Space, resulting in a significant scaling problem, e.g $\binom{4}{2} = 6$, $\binom{10}{5} = 252$, $\binom{20}{10} = 184,765$.

As a result of this scaling problem, the ED method is limited to small systems.

2.1.2 On-site Occupation

Following ED, the on-site occupations of the system in a given state, (e.g the ground-state) can be found. The on-site occupation for site i , for a given energy level E_m is given by,

$$n_i^m = \langle \psi^m | \hat{n}_i | \psi^m \rangle. \quad (9)$$

The set of on-site occupations, for each eigenstate, form the electron density.

2.1.3 Kinetic and Potential Energies

For a given eigenstate $|\psi^m\rangle$ with a corresponding energy E_m and on-site occupations $[n_1^m, n_2^m, n_3^m, \dots, n_{L-1}^m, n_L^m]$, the total potential energy is,

$$U_{Total} = \langle \psi^m | U \sum_i^L \hat{n}_i \hat{n}_{i+1} | \psi^m \rangle. \quad (10)$$

$|\psi^m\rangle$ being a linear combination of the basis states.

The total on-site and kinetic energies are computed in similar fashion.

2.2 Density Functional Theory

The two Hohenberg-Kohn Theorems provide the foundation of DFT.

2.2.1 Theorem 1: Existence of a universal functional

For any system of N interacting electrons moving under the influence of an external potential, $v_{ext}(\mathbf{r})$, (e.g. that of the nuclei) the external potential, and hence the total energy, is a unique functional of the electron density $n(\mathbf{r})$.

The total energy of the system can be written as,

$$E[n(\mathbf{r})] = \int n(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]. \quad (11)$$

Where $F[n(\mathbf{r})]$ is universal, namely it is independent of the system. A corollary of the first Hohenberg-Kohn theorem is that there is a one-to-one correspondence between the external potential $v_{ext}(\mathbf{r})$ and the electron density $n(\mathbf{r})$, meaning that one is sufficient to determine the other.

2.2.2 Theorem 2: Variational Principle

The second theorem establishes the variational principle, namely it states that the universal functional is minimised at the ground state density $n(\mathbf{r})_{GS}$, and the corresponding energy is the groundstate energy, E_{GS} . In mathematical terms this means that,

$$E_{GS} = E[n(\mathbf{r}_{GS})] \leq E[n(\mathbf{r})]. \quad (12)$$

The dimension of the wavefunction of a many-body problem typically scales very badly. Whereas the electron density is at most a function of 3 spatial coordinates. The strength of DFT lies in needing to solve for the electron density rather than the wavefunction.

However, the universal functional is unknown and needs to be approximated. DFT has been widely applied to various quantum mechanical systems.....

3 Plan

- work on script that does ED.
- FOCUS ON SPIN CASE AS THIS IS WHAT THEY DO IN THE PAPER
- Can rewrite the script for spinless case in future if too computationally expensive for a larger system

- Python script that generates and solves the general Hubbard Hamiltonian Matrix exactly (ED). script should return the relevant ground-state density $\{n_i^{GS}\}$ with the corresponding DFT functional $F[n_i^{GS}] = E^{GS} - \sum_i n_i^{GS} \epsilon_i$. Given $\{\epsilon\}$ as input.

4 Code

4.1 1D with Spin

Normal 1D Hubbard model is:

$$\mathbf{H}_{Spin} = \sum_{i,\sigma}^L \epsilon_i \hat{a}_{i,\sigma}^\dagger \hat{a}_{i,\sigma} - t \sum_{i,\sigma}^L \hat{a}_{i,\sigma}^\dagger \hat{a}_{i+1,\sigma} + U \sum_i^L \hat{n}_{i,\downarrow} \hat{n}_{i,\uparrow}$$

4.2 Matrix generation: Steps

Write function that creates the Hamiltonian matrix, given inputs

[Length_of_chain, N_\uparrow , N_\downarrow , U , t , external potential $\{\epsilon_i\}$]

1. Generate basis states, taking combination of spin up and spin downs
2. Use binary representation of basis state, e.g for a state $|0, 1, 0, 1\rangle \rightarrow 5$, storing states as integers.
3. Calculate matrix entries via fast bitwise operations, as searching through Numpy arrays for hopping terms is complicated and expensive.

4.3 Bitwise operations

4.3.1 XOR

have basis states $|0, 1, 1, 0\rangle$ and $|1, 0, 1, 0\rangle$, taking XOR and summing gives

$$sum(|1, 1, 0, 0\rangle) = 2$$

When the sum is equal to 2 we have a hopping term

$$H_T[|0, 1, 1, 0\rangle, |1, 0, 1, 0\rangle] = -t$$

This is for the spinless case, but is identical for the case with spin.

4.3.2 AND operation for Coulomb Potential

Will store basis states with the first half of bits representing spin-up and the second representing spin-down, e.g

$$|0011; 1001\rangle$$

Then by taking AND of this states spin separated parts, we get the Coulomb repulsion term

$$sum(0011 \text{ } AND \text{ } 1001) = 1$$