

1 Introduction

One of the most important basic problems in physics is the dynamics of many-body system. Specifically, in quantum physics and chemistry, the dynamics of electrons and their spatial distribution determine the stability of matter. But it is not just the stability that matters. Electronic structure of materials determines many macroscopic properties like thermal and electrical conductivity, their response to electronic and magnetic field, etc.

Calculation of electronic structure has always been a challenge. It quickly became apparent that direct use of schroedinger equation is not a realistic prospect for calculation of electronic structure, except for some small molecules, as it's time complexity grows exponentially as a function of electron number. With the development of computers different numerical schemes for computation of electronic structure and optimization of molecular structure have emerged. One of them is also density functional theory (DFT from now on), which has been known for roughly 50 years. Through the years DFT has developed and today it represents one of the main tools for calculation of electronic structure especially for complex molecules and crystals.

2 Matter description

Physical description of matter surrounding us is given by hamiltonian:

$$H = T_n + T_e + W_{n-n} + W_{e-e} + W_{n-e} + V_{ext}, \quad (1)$$

where T_n and T_e are kinetic energies of nuclei and electrons respectively, W_{n-n} , W_{e-e} and W_{e-n} represent nuclei-nuclei, electron-electron and electron-nuclei interaction terms. V_{ext} represents external potential. Ground state of such system is given by the solution of time independant Schroedinger equation:

$$\hat{H}\psi = \epsilon_0\psi_0, \quad (2)$$

where index 0 denotes the solution with the lowest energy. In general ψ_0 depends on $3N$ coordinates, where N is total number of particles. This means that complex systems with more than e.g. 10 atoms are very computationally demanding. It is common to reduce the dimensionality of the problem by employing Born-Oppenheimer approximation in which nuclei have fixed positions.

3 Density functional theory

DFT is a method, which allows us to replace operator, which operate on wavefunctions, with operators which depend only on density of particles of particular spin. The core of dft lies in Kohn-Sham theorems. These two theorems ensure that stationary many-particle systems are fully characterized by their ground state density. For non-degenerate case the latter is uniquely determined by many-particle wave function, which in turn is uniquely determined by the external potential. For a simple non-degenerate case we will prove this theorem. Let us consider hamiltonian of the form:

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}_{ext}, \quad (3)$$

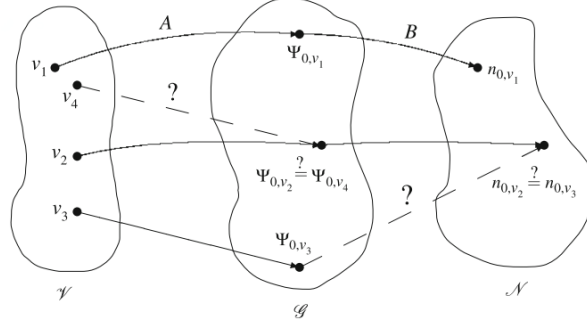


Figure 1: Bijection between the set of potentials, their corresponding ground states and ground state densities. Existence of such bijection is proved by Kohn-Sham theorems and proves that multi-particle system is uniquely determined by its ground state particle density.

where T is kinetic energy, W is particle interaction and V is external potential determined up to a constant. Let V_{ext} be such potential that ground state ψ_0 is non-degenerate. Consider now the set of all H of the form (3), which differ only in V_{ext} , with non-degenerate ground state. Since kinetic and inter-particle interaction terms are the same for all H in such set, the latter can be represented by the set of all non-equivalent potentials:

$$\mathcal{V} = \{V_{ext}; \quad V \text{ determined up to multiplication factor and a constant;} \\ |\psi_0\rangle \text{ exists and is non-degenerate}\} \quad (4)$$

According to the above definition we can define the set of all corresponding ground state-densities determined up to phase as:

$$\mathcal{G} = \{\psi_0; \quad \psi_0 \text{ ground state corresponding to a potential from } V; \\ \psi_0 \sim \psi_0 e^{i\phi}\} \quad (5)$$

The map from \mathcal{V} to \mathcal{G} is surjective by definition. What we would like to know is if it is also injective 1, i.e. can a single ψ_0 be a ground state for two non-equivalent potentials? Suppose now that ψ_0 is a ground state for two non-equivalent potentials V_{ext} and V'_{ext} .

$$\hat{H} |\psi_0\rangle = (\hat{T} + \hat{W} + \hat{V}_{ext}) |\psi_0\rangle = \epsilon_0 |\psi_0\rangle, \quad (6)$$

$$\hat{H}' |\psi_0\rangle = (\hat{T} + \hat{W} + \hat{V}'_{ext}) |\psi_0\rangle = \epsilon'_0 |\psi_0\rangle, \quad (7)$$

subtracting above equation yields:

$$(\hat{V}_{ext} - \hat{V}'_{ext}) |\psi_0\rangle = (\epsilon_0 - \epsilon'_0) |\psi_0\rangle. \quad (8)$$

due to multiplicative nature of potentials, we can just divide the whole equation by $|\psi_0\rangle$ and obtain:

$$(\hat{V}_{ext} - \hat{V}'_{ext}) = (\epsilon_0 - \epsilon'_0), \quad (9)$$

which is contradiction, since our