

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

Non-relativistic hamiltonian describing the interaction system on nuclei and electrons can be written as follows:

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{W}_{n-n} + \hat{W}_{e-e} + \hat{W}_{n-e} + \hat{V}_{ext}, \quad (1)$$

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 and is strictly of multiplicative nature. Ground state of such system is given by the solution of time independent Schrödinger 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 motion of nuclei is separated from motion of electrons, sometimes even fixed. Thus, from now on we will restrict ourselves to hamiltonian describing only motion of electrons:

$$\hat{H} = \hat{T}_e + \hat{W}_{e-e} + \hat{W}_{n-e} + \hat{V}_{ext}. \quad (3)$$

The number of electrons N for a small molecules, like water, is of the order ~ 10 . In medium sized molecules with $\sim 50 - 100$ atoms, the number can grow to a few hundred, while in large molecules, like proteins, the number can grow into thousands and ten-thousands. As one can imagine, solving a system of coupled differential equations with such huge number of coordinates ($3N$) is still too big problem for present computational power. This is the reason for development of approaches which while still being sufficiently accurate, offer faster computational times. In this paper we will discuss dft and it's applications to organo-metalic materials.

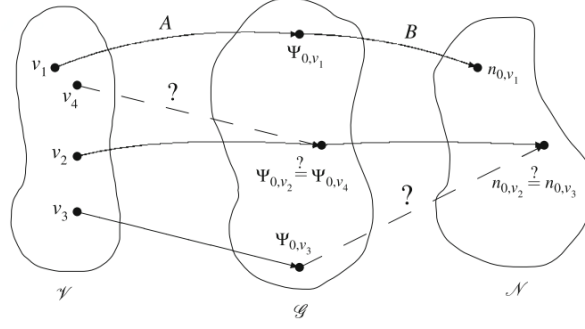


Figure 1: Bijection between the set of potentials, their corresponding ground states and ground state densities. Existence of such bijection is proved by Kohn-Sham theorems and proves that multi-particle system is uniquely determined by its ground state particle density.

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:

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}_{ext}, \quad (4)$$

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 (4), 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:

$$\mathcal{V} = \{V_{ext}; \quad V \text{ determined up to multiplication factor and a constant}; \\ |\psi_0\rangle \text{ exists and is non-degenerate}\} \quad (5)$$

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

$$\mathcal{G} = \{\psi_0; \quad \psi_0 \text{ ground state corresponding to a potential from } \mathcal{V}; \\ \psi_0 \sim \psi_0 e^{i\phi}\} \quad (6)$$

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} .

$$\hat{H} |\psi_0\rangle = (\hat{T} + \hat{W} + \hat{V}_{ext}) |\psi_0\rangle = \epsilon_0 |\psi_0\rangle, \quad (7)$$

$$\hat{H}' |\psi_0\rangle = (\hat{T} + \hat{W} + \hat{V}'_{ext}) |\psi_0\rangle = \epsilon'_0 |\psi_0\rangle, \quad (8)$$

subtracting above equation yields:

$$(\hat{V}_{ext} - \hat{V}'_{ext}) |\psi_0\rangle = (\epsilon_0 - \epsilon'_0) |\psi_0\rangle. \quad (9)$$

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

$$(\hat{V}_{ext} - \hat{V}'_{ext}) = (\epsilon_0 - \epsilon'_0), \quad (10)$$

which is contradiction, since V_{ext} and V'_{ext} differ for more than a constant. Similarly one can show that two different ground state wave functions, corresponding to two different external potentials, cannot lead to the same ground state densities. To see this we compare ground state energies and rewrite them using ground state density, which is supposed to be the same for both wavefunctions:

$$\begin{aligned} \langle \psi_0 | \hat{H} | \psi_0 \rangle = \epsilon_0 &< \langle \psi'_0 | \hat{H} | \psi'_0 \rangle = \langle \psi'_0 | \hat{H} + \hat{V}'_{ext} - \hat{V}'_{ext} | \psi'_0 \rangle = \\ &\epsilon'_0 + \langle \psi'_0 | \hat{V}_{ext} - \hat{V}'_{ext} | \psi'_0 \rangle. \end{aligned} \quad (11)$$

Rewriting this in terms of densities and taking into account equivalence of H and H' yields:

$$\epsilon_0 < \epsilon'_0 + \int (V_{ext}(\mathbf{r}) - V'_{ext}(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}, \quad (12)$$

$$\epsilon'_0 < \epsilon_0 + \int (V'_{ext}(\mathbf{r}) - V_{ext}(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}. \quad (13)$$

Upon subtracting both equations one obtains a contradiction:

$$\epsilon_0 + \epsilon'_0 < \epsilon_0 + \epsilon'_0, \quad (14)$$

which proves that for hamiltonians which yield non-degenerate ground states, each ground state leads to a different ground state particle density. Ground state particle densities form a set where each density corresponds to a single wave function from \mathcal{G} :

$$\mathcal{N} = \{n; \langle \psi | \hat{n} | \psi \rangle, \psi \in \mathcal{G}\}, \quad (15)$$

where \hat{n} is quantum mechanical particle density operator.

Extension of this simple prove to hamiltonians with degenerate ground states is possible by replacing ground state wave functions by linear span of degenerate ground states. Thus in degenerate case one obtains bijection between external potential, set of linear spans, each belonging to a certain external potential and a set of sets of ground state densities. Special treatment is necessary also for systems containing magnetic fields, where one can separate hamiltonian into two hamiltonians (one for each spin) of the form 4.

Since there exists bijection between ground state wave functions and ground state densities, one can formally rewrite ground state wave functions as functionals of ground state particle density:

$$|\psi'_0\rangle = |\psi'_0[n]\rangle, \quad (16)$$

and using above formula one can also rewrite operators in terms of ground state density. As an example, let us rewrite ground state energy as functional of ground state particle density:

$$E[n_0] = \langle \psi_0[n_0] | \hat{H} | \psi_0[n_0] \rangle. \quad (17)$$

Further, one can define more general energy functional:

$$E[n] = \langle \psi[n] | \hat{H} | \psi[n] \rangle, \quad (18)$$

for which one can find minimum energy principle: $E[n_0] < E[n]$ whenever n belongs to \mathcal{N} . This is an obvious consequence of wave function functional $|\psi[n]\rangle$, which is only defined for densities which are in \mathcal{N} . In practice this is not such a problem. The reason for this is discretization of space into grid points. On final grid for any strictly positive particle density ($n(\mathbf{r}) > 0$), which is compatible with Pauli principle, there exists a potential for which the density represents ground state density and is thus contained in \mathcal{N} .

One can also show that $E[n]$ be reasonably extended, to a larger set of densities $n(\mathbf{r})$. Since the Hamiltonian 4 is defined for all