

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. One of the most used theory today is density functional theory.

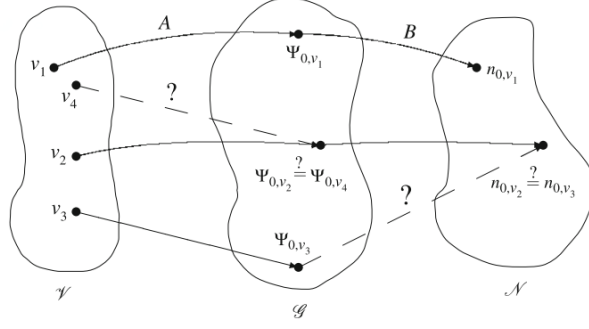


Figure 1: Bijection between the set of potentials, their corresponding ground states and ground state densities. Existence of such bijection is proved by Kohn-Sham theorems and proves that multi-particle system is uniquely determined by its ground state particle density.

3 Density functional theory - DFT

DFT is a method, which allows us to map many-particle problem to a single particle problem. It effectively replaces electron wave functions with particle density. 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 particle density. For non-degenerate case the latter is uniquely determined by ground state 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:

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

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} .

To see that something similar also holds in general, one has to show, that suitable wavefunctions can be constructed from a set of non-negative, normalizable densities. Solutions to hamiltonian of the form 3 are anti-symmetric N -particle wave functions. Each such wave function represents a ground state corresponding to a certain potential and for each such wavefunction one can find particle density simply by applying quantum-mechanical particle density operator. But more importantly, the conversely is also true. From each non-negative particle density $n(\mathbf{r})$, one can construct N particle antisymmetric wavefunction as follows:

$$\Phi_k(\mathbf{r}) = \sqrt{\frac{n(\mathbf{r})}{N}} e^{i[\mathbf{k} \cdot \mathbf{f}(\mathbf{r}) + \phi(\mathbf{r})]}; \quad k \in \mathbb{Z}, \quad (18)$$

where $\phi(\mathbf{r})$ is an arbitrary scalar function and $f(\mathbf{r})$ is a vector field given by:

$$f_x(\mathbf{r}) = 2\pi \frac{\int_{-\infty}^x dx' n(x', y, z)}{\int_{-\infty}^{\infty} dx' n(x', y, z)} \quad (19)$$

$$f_x(\mathbf{r}) = 2\pi \frac{\int_{-\infty}^{\infty} dx' \int_{-\infty}^y dy' n(x', y', z)}{\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' n(x', y', z)} \quad (20)$$

$$f_x(\mathbf{r}) = 2\pi \frac{\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^z dz' n(x', y', z')}{\int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_{-\infty}^{\infty} dz' n(x', y', z')}. \quad (21)$$

Using Slater determinant one can now construct N -particle wave function from $\phi_k(\mathbf{r})$:

$$\Phi_k(\mathbf{r}) = \frac{1}{\sqrt{N}} S_- (\phi_1 \phi_2 \dots \phi_N). \quad (22)$$

Above discussion tells us that minimization principle indeed holds for all non-negative, normalizable densities, but it says nothing about definiteness of functional. For a given functional to be even defined for given particle density, the following has to hold separately:

$$\langle \psi | \hat{T} | \psi \rangle < \infty \quad (23)$$

$$\langle \psi | \hat{W} | \psi \rangle < \infty \quad (24)$$

$$\langle \psi | \hat{V} | \psi \rangle < \infty. \quad (25)$$

After deeper mathematical analysis of above equations, one can deduce that both ψ and $n^{1/2}$ have to be from Sobolev space defined by:

$$\mathbb{H} = \{f; f \in \mathbb{L}^2 \text{ and } \nabla f \in \mathbb{L}^2\}, \quad (26)$$

where \mathbb{L} is a space of functions with finite second norm. Equations 23 and 24 have imposed restrictions on permissible wavefunctions and densities. Equation 25 also imposes restriction on potentials. They should be of the form $\mathbb{L}^{3/2} + \mathbb{L}^\infty$, thus every potential should consist of a part with a finite ∞ -norm and a part with a finite $3/2$ -norm. As it turns out, the coulomb potential satisfies all requirements.

3.1 All electron dft calculations

All electron dft calculation is mostly used to calculate electronic structure of a single molecule. The molecule should not be too big, as otherwise the problem may become too computationally expensive.

3.2 Dft using pseudopotentials

Electronic states of an atom can be divided into three categories; core states, semi-core states and valence states. The latter are the most actively included in formation of bonds. Valence states may be completely deformed once the atom is put into molecules/crystals. Semi-core state are states which do not directly contribute to bonding, but may still be polarized or spatially deformed. Lastly, core states, are highly localized and are assumed to be unaffected by chemical bonding. This means that there should be very little loss of accuracy if core states are replaced by a pseudo wavefunction. Pseudopotentials are constructs which try to replicate effects of core electrons exerted on semi-core, valence electrons and thus reproduce correct chemical and physical properties (bonding energy, bond length, electron localization, magnetization,...).

Of course, pseudo potentials are constructed prior to a given calculation. Thus, they have to be constructed using some other information. As a consequence, there exists a question of transferability. Is a potential constructed using some reference molecule usable for another molecule. The exact answer is not possible. Many times the only way is to try, especially when transition elements are in question.

4 Dft in crystals

Crystals are periodic structures. This fact is also reflected the shape of electronic wave functions, which are Bloch states:

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}; \quad u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n,\mathbf{k}}(\mathbf{r}), \quad (27)$$

where \mathbf{R} is a vector in Bravais lattice of a crystal in question. Functions $u_{n,\mathbf{k}}$ depend on potential at each atomic site. In ideal case, where core potentials are neglected, wave functions are simple plane waves. When potential is weak and reasonably smooth, it can be treated as perturbation. Unfortunately neither of the two conditions is true. Core potential diverges as $r \rightarrow 0$ and as a consequence the wave functions have a cusp at the origin. For heavier atoms core states have large gradients and can not be represented as plane waves.

The simplest solution is to expand wave functions into series of plane waves. Computationally this is just a discrete fourier transform of a wave function. However, because of already given reasons, the number of plane waves required for such expansion is very large. Thus, even the sum of plane waves is not a suitable representation of core states. For this reason, core states are commonly replaced by pseudo potentials in crystal dft calculations. This approach usually carries *PW calculation* designation.

Although, for many crystals this approach works well it is not good enough especially for transition elements with partially filled d-shells and second row elements. Electron density of transition metals and second row elements still varies widely in

spite of use of pseudopotentials. For such cases an improved approach has been developed. A new method, called gaussian augmented plane waves or *GAPW* approach. *GAPW* basis sets consist of Gaussian functions and plane waves. This approach is suitable for all electron calculations, where core states are expanded in Gaussian functions and valence electrons in plane waves. As a consequence, all electron wave calculations are possible for crystals avoiding pseudo potential inaccuracy issues.