1 Introduction

One of the most important basic problems in physics is the dynamics of many-body systems. Specificaly, 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 fields, etc.

Calculation of electronic structure has always been a challenge. It quickly became apparent that direct use of Schrödinger equation is not a realistic prospect for calculation of electronic structure, except for some small molecules, as the time consumed to solve it grows exponentially [1] as a function of electron number. With the development of computers different numerical approximations for computation of electronic structure and optimization of molecular structure have emerged. One of the most successful methods has been 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 Hamilotnian

The first step in formulation of the problem is to define hamiltonian which describes motion of nuclei and electrons. Non-relativistic hamiltonian describing the interaction of nuclei and electrons can be written as follows:

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

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} is strictly multiplicative external potential. Ground state of such system is given by the solution of time independent Schrödinger equation:

$$\hat{H}\psi = \epsilon_0 \psi_0, \tag{2}$$

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 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 the motion of nuclei is separated from motion of electrons, sometimes even fixed. Thus, from now on we will restrict ourselves to hamiltonians describing only the motion of electrons:

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

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 computationally

very intensive procedure and not suitable for mass research usage. This is the reason for development of approaches which, while still being sufficiently accurate, offer faster computational times. DFT represents one of the most successful methods to solving such systems.

3 Density functional theory - DFT

DFT is a method, which allows us to map many-particle problem to an effectively single particle problem. It replaces all electron wave function 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:

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}_{ext}, \tag{4}$$

where T is kinetic energy, W is inter-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 states. 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:

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

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

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

The map from $\mathcal{V}$ to $\mathcal{G}$ is surjective by definition. What we would like to know is, if it is also injective (2), 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}.

$$\hat{H} |\psi_0\rangle = (\hat{T} + \hat{W} + \hat{V}_{ext}) |\psi_0\rangle = \epsilon_0 |\psi_0\rangle, \tag{7}$$
$$\hat{H}' |\psi_0\rangle = (\hat{T} + \hat{W} + \hat{V}'_{ext}) |\psi_0\rangle = \epsilon'_0 |\psi_0\rangle, \tag{8}$$

subtracting above equation yields:
$$(\hat{V}_{ext} - \hat{V}'_{ext}) |\psi_0\rangle = (\epsilon_0 - \epsilon'_0) |\psi_0\rangle. \tag{9}$$

due to multiplicative nature of potentials, we can just divide the whole equation by $|\psi_0\rangle$ and obtain:
$$(\hat{V}_{ext} - \hat{V}'_{ext}) = (\epsilon_0 - \epsilon'_0), \tag{10}$$

which is contradiction, since must V_{ext} and V'_{ext} differ for more than a constant. Similarly one can show that two different grounds state wave functions, corresponding
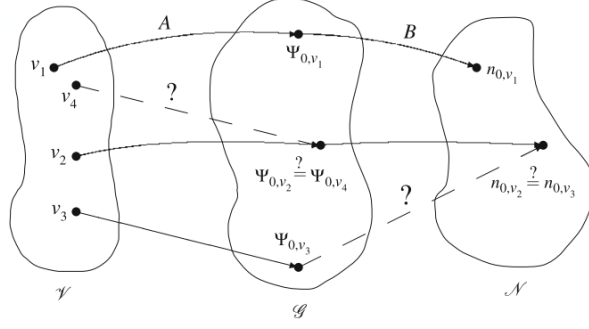
Figure 1: Bijection between the set of potentials, their corresponding ground states and ground state densities. Existance of such bijection is proven by Kohn-Sham theorems and proves that multi-particle system is uniquely determined by it's ground state particle density [2].

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 densities, which is supposed to be the same for both wave functions:

$$\langle \psi_o | \hat{H} | \psi_0 \rangle = \epsilon_0 < \langle \psi'_o | \hat{H} | \psi'_0 \rangle = \langle \psi'_o | \hat{H} + \hat{V}'_{ext} - \hat{V}'_{ext} | \psi'_0 \rangle = \qquad (11)$$
$$\epsilon'_0 + \langle \psi'_o | \hat{V}_{ext} - \hat{V}'_{ext} | \psi'_0 \rangle \, .$$

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

$$\epsilon_0 < \epsilon'_0 + \int \left(V_{ext}(\boldsymbol{r}) - V'_{ext}(\boldsymbol{r}) \right) n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}, \qquad (12)$$

$$\epsilon'_0 < \epsilon_0 + \int \left(V'_{ext}(\boldsymbol{r}) - V_{ext}(\boldsymbol{r}) \right) n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}. \qquad (13)$$

Upon subtracting both equations one obtains a contradiction:
$$\epsilon_0 + \epsilon'_0 < \epsilon_0 + \epsilon'_0, \qquad (14)$$

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 $\mathcal{G}$:

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

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 spin up and spin down hamiltonian of the form (4). In the latter case one can obtain bijections between the set of pairs $(\boldsymbol{A}(\boldsymbol{r}), V_{ext}(\boldsymbol{r}))$, $(\psi_\uparrow, \psi_\downarrow)$ and $(n(\boldsymbol{r}), \boldsymbol{m}(\boldsymbol{r}))$.

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

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

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:

$$E[n_0] = \langle \psi_0[n_0]| \, \hat{H} \, |\psi_0[n_0]\rangle \, . \tag{17}$$

for which one can find minimum energy principle: $E[n_0] < E[n]$ whenever n belongs to $\mathcal{N}$. This an obvious consequence of wave function functional $|\psi[n]\rangle$, which is only defined for densities which are in $\mathcal{N}$. Thus, one has to ask himself whether every nonegative normalizable function $n(\boldsymbol{r})$ is in $\mathcal{N}$. The answer is no. A density from $\mathcal{N}$ have a corresponding potential V_{ext} such that it minimizes energy functional of the form 17 and consequently they are called V-representable densities.

In practice, one does not need deep knowledge about such mathematical definitions of functionals. The reason for this is the discretization of space into grid points. On final grid for any strictly positive particle density $(n(\boldsymbol{r}) > 0)$, which is compatible with Pauli principle, there exists a potential for which the density represents ground state density and is thus contained in $\mathcal{N}$ [2].

The set $\mathcal{N}$ is not know and to ensure the problem is also mathematically well defined, one has to make a transition from v-representability to N-representability. Let us first redefine our problem in the form of Levy-Lieb functional:

$$E_{LL}[n] = F_{LL}[n] + \int V_{ext}(\boldsymbol{r})n(\boldsymbol{r}) \tag{18}$$

$$F_{LL} = \inf_{\psi \to n} \langle \psi| \, \hat{T} + \hat{W} \, |\psi\rangle \, , \tag{19}$$

where $\psi \to n$ means that infimum has to be taken over all N-particle wave functions, i.e. over all N-representable densities. Levy-Lieb functional is an extension of Kohn-Sham energy functional and it has a minimum for exactly the same electron density $n(\boldsymbol{r})$ [2]:

$$E_0 = \min_{n} \left(\inf_{\psi \to n} \langle \psi| \, \hat{H} + \hat{W} + V_{ext} \, |\psi\rangle \right) \tag{20}$$
$$= E_{LL}[N].$$

The set of v-representable densities is a subset of N-representable densities, since not all N-electron wave functions necessarily represent ground state for some external potential V_{ext} [3].

The next very important result is that one can construct N-electron anti-symmetric wave function from every non-negative, normalizable function $n(\boldsymbol{r})$ [2, 3]. Thus, Levy-Lieb functional is, in principle, well defined for any non-negative, normalizable function $n(\boldsymbol{r})$.

To construct an anti-symmetric N-electron wave function one can use the following procedure [2, 3]:

$$\Phi_k(\boldsymbol{r}) = \sqrt{\frac{n(\boldsymbol{r})}{N}} e^{i[\boldsymbol{k}\cdot\boldsymbol{f}(\boldsymbol{r})+\phi(\boldsymbol{r})]}; \quad k \in \mathbb{Z}, \tag{21}$$

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

$$f_x(\boldsymbol{r}) = 2\pi \frac{\int_{-\infty}^{x} \mathrm{d}x' n(x', y, z)}{\int_{-\infty}^{\infty} \mathrm{d}x' n(x', y, z)} \tag{22}$$

$$f_x(\boldsymbol{r}) = 2\pi \frac{\int_{-\infty}^{\infty} \mathrm{d}x' \int_{-\infty}^{y} \mathrm{d}y' n(x', y', z)}{\int_{-\infty}^{\infty} \mathrm{d}x' \int_{-\infty}^{\infty} \mathrm{d}y' n(x', y', z)} \tag{23}$$

$$f_x(\boldsymbol{r}) = 2\pi \frac{\int_{-\infty}^{\infty} \mathrm{d}x' \int_{-\infty}^{\infty} \mathrm{d}y' \int_{-\infty}^{z} \mathrm{d}z' n(x', y', z')}{\int_{-\infty}^{\infty} \mathrm{d}x' \int_{-\infty}^{\infty} \mathrm{d}y' \int_{-\infty}^{\infty} \mathrm{d}z' n(x', y', z')}. \tag{24}$$

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

$$\Phi(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \det\left(\phi_1 \phi_2 ... \phi_N\right). \tag{25}$$

Above discussion tells us that minimization principle indeed holds for all non-negative, normalizable densities, but it says nothing about definitness of functional. For a given functional to be even defined for given particle density, the following has to hold separately [2]:

$$\langle \psi | \hat{T} | \psi \rangle < \infty \tag{26}$$

$$\langle \psi | \hat{W} | \psi \rangle < \infty \tag{27}$$

$$\langle \psi | \hat{V} | \psi \rangle < \infty. \tag{28}$$

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

$$\mathcal{H} = \left\{ f; f \in \mathcal{L}^2 \text{ and } \nabla f \in \mathcal{L}^2 \right\}, \tag{29}$$

where $\mathcal{L}$ is a space of functions with finite second norm. The of N-representable densities is now known exactly:

$$\mathcal{N} = \left\{ n; \int n(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} = N; n \in \mathcal{H} \text{ and } 0 \leq n(\boldsymbol{r}) \right\}, \tag{30}$$

Equations 26 and 27 have imposed restrictions on permissible wavefunctions and densities. Equation 28 also imposes restriction on potentials. They should be of the form $\mathcal{L}^{3/2} + \mathcal{L}^{\infty}$, 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 coluomb potential satisfies all requirements.

3.1   Variational formualtion

4   Kohn-Sham equations

After establishing validity of the transition from single particle wave functions to particle density, we can now finally formulate out problem using $E[n]$. We are looking for a minimum value of energy functional $E[n]$ with respect to particle density n. Thus, what we have is an extremal problem:

$$\frac{\delta}{\delta n(\boldsymbol{r})} \left[E[n(\boldsymbol{r})] - \mu \left(\int n(\boldsymbol{r}) - N \right) \right] = 0. \tag{31}$$

$E[n]$ is unfortunately still defined only formally by $E[n] = \langle \psi[n] | H | \psi[n] \rangle$. To actually solve the equation 31, we have to define $E[n(\boldsymbol{r})]$ in terms of particle density $n(\boldsymbol{r})$.

4.1   Noninteracting system

First let's have a look at the hamiltonian of N-particle non-interacting system

$$\hat{H} = \hat{W}_k + \hat{V}_{ext}, \tag{32}$$

where V_{ext} is an external potential of multiplicative nature. The solution to this problem can be written in the form of Slater determinant:

$$|\Phi_0\rangle = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \phi_1(\boldsymbol{r}_1, \sigma_1) & \phi_2(\boldsymbol{r}_1, \sigma_1) & \phi_3(\boldsymbol{r}_1, \sigma_1) & \dots & \phi_N(\boldsymbol{r}_1, \sigma_1) \\ \phi_1(\boldsymbol{r}_2, \sigma_2) & \phi_2(\boldsymbol{r}_2, \sigma_2) & \phi_3(\boldsymbol{r}_2, \sigma_2) & \dots & \phi_N(\boldsymbol{r}_2, \sigma_2) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_1(\boldsymbol{r}_N, \sigma_N) & \phi_2(\boldsymbol{r}_N, \sigma_N) & \phi_3(\boldsymbol{r}_N, \sigma_N) & \dots & \phi_N(\boldsymbol{r}_N, \sigma_N) \end{bmatrix},$$

which, when inserted into equation (32) effectively produces single particle problem:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + \hat{V}_{ext}(\boldsymbol{r}) \right) \psi(\boldsymbol{r}) = \epsilon_i \psi(\boldsymbol{r}). \tag{33}$$

Thus, using slater determinant we have effectively converted many particle problem with $3N$ coordinates to a single particle problem, which is the same as many-particle non-interacting system. The ground state of such a system is obtained using $N/2$ lowest states and putting 2 electrons into each state. Calculation of kinetic energy and particle density for such a system is also straight forward. As we can see, using Slater determinant as ansatz for the solution of noninteracting hamiltonian offers simple expressions for ground state wavefunction, kinetic energy and particle density calculation.

Now we would like to use similar construction to solve hamiltonian 17. Using solution ansatz in the form of Slater determiant or some other sum of basis functions (commonly called orbitals) offers straight forward calculation of kinetic energy and particle density. It might be worth to point out that dft packages usually do not use Slater determinant to construct wavefunctions and calculate density. Using Slater determinant leads to differential equations for ϕ_k wavefunctions. Instead, they usually use large sets of basis functions, which in the end lead to eigenvalue problem. Solution is then given by populating lowest energy orbitals until all electrons are allocated.

First we have to ask ourselves if it is at all possible to convert interacting N particle problem ($3N$ coordinates) to a single particle (3 coordinates) problem. To see how this is possible consider a N particle interacting system with $n(\boldsymbol{r})_{i0}$ ground state particle density. Since it represents ground state, this particle density belongs to $\mathcal{H}$. Further, using equation (25) one can construct non-interacting many particle wave function, which minimizes hamiltonian of the form (32) for some potential V_{ext}. Such system is called Kohn-Sham system. Thus, we see that there exists a non-interacting system with exactly the same ground state particle density as originally considered interacting system. The question still remains what kind of potential should one use in place of many particle interaction operators still remains open.

Intuitively, one would expect that potential belonging to effective single particle hamiltonian should reflect the properties, geometry and potentials found in given many particle system. Hamiltonian naturally contains kinetic energy term, but it should also somehow contain inter particle interactions. These should again be functionals of inter particle interaction (coulomb repulsion),

4.2 Exchange and correlation functionals

Exchange and correlation functionals are functionals which try to account for exchange and correlation interactions between particles. They can be of a different forms and in general one can roughly divide them into 4 groups [4]:

4.2.1 Lda

Local density approximation (lda) are functionals which depend only on density of particles (electrons) [4]. First functional of such form dates back into the year 1930, when the exchange interaction for uniform gas was discovered [4]:

$$E_{xc}^{lda}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n(\boldsymbol{r})^{4/3}. \tag{34}$$

Today, there exist multiple other lda exchange functionals, but for most cases they are not very useful. Their only advantage are fast computational times. For every other purpose gga and hybrid functionals are much better suited.

4.2.2 Gga

Generalized gradient approximation (gga) functionals depend not only on density of particles but also on its gradient [4]. Most commonly, gga functionals are build upon (34) [4]:

$$E_{xc}^{gga} = \int n(\boldsymbol{r})^{4/3}F(x); \quad x = |\nabla n(\boldsymbol{r})|/n(\boldsymbol{r})^{4/3}. \tag{35}$$

One of most commonly used gga functional is PBE functional [4] [4]:

$$E_{xc}^{pbe} = -\int n(\boldsymbol{r})^{4/3}\left[\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} + \frac{\mu s}{1 + \mu s^2/\kappa}\right]; \quad s = x/(2(3\pi/2)^{1/3}). \tag{36}$$

Gga functionals offer acceptable accuracy at fast computational times and are most commonly used for approximate calculation, before starting more accurate and more time consuming calcualtion using hybrid or meta-gga functionals.

4.2.3 Meta-gga functionals

Since gga functionals have their short commings, meta-gga functionals were formed in belief that adding higher derivatives will improve accuracy [4]. Meta-gga functionals are build upon gga functional form and add terms containing higher order derivatives of particle density. Functionals are formulated according to the following equation [4]:

$$E_{xc}^{MGGA} = \int \rho^{4/3}F(\rho(\boldsymbol{r})\nabla\rho(\boldsymbol{r}), \nabla^2\rho(\boldsymbol{r}), \tau(\boldsymbol{r})); \quad \tau = \frac{1}{2}\sum_i |\nabla\phi_i(\boldsymbol{r})|^2 \tag{37}$$
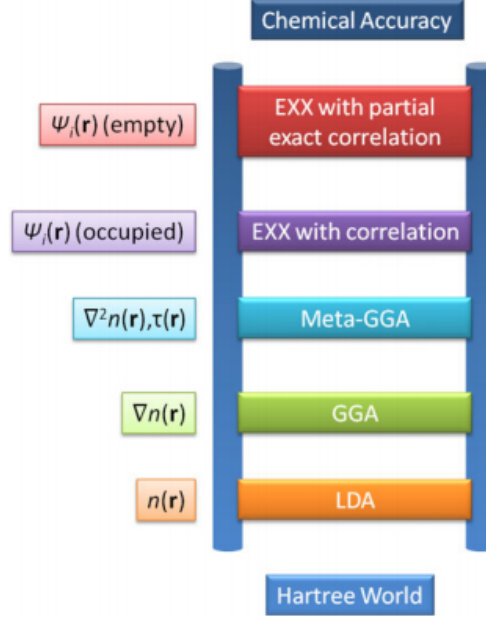
Figure 2: Jacob's ladder of exchange-correlation functional approximations employed in dft calculations. Hartree world represents starting level where only weak interparticle interaction is present. Lda approxiamtion covers functionals which depend only on particle density. Gga additionally depends on gradient of particle density, while mega-gga incorporates higher order derivatives of particle density and in some cases even kinetic energy of orbitals (τ). Hyper-gga functionals, also called hybrid functionals, stage represents functionals which contain exact exchange calculation (i.e. the one found in Hartree-Fock method). The last level utilizes all Kohn-Sham orbitals to calculate correlation and exchange interaction. This level also accounts for VdW interaction, which is caused by charge fluctuations and is not accounted for in previous stages [5].

Meta-gga functionals have higher computational cost than gga functionals Unfortunately, as it turned out, they are not significantly better than gga functionals and are thus not so popular.

4.2.4 Hybrid functionals

On the contrary to meta-gga functionals, hybrid functionals are much more successful [4]. These functionals are not a continuation of lda, gga, meta-gga chain. Instead they incorporate exact Hartree-Fock exchange term [4]:

$$E_{xc}^{hf} = \sum_{i,j,\sigma} \int \frac{\phi_{i\sigma}^*(\boldsymbol{r})\phi_{j\sigma}(\boldsymbol{r})\phi_{j\sigma}^*(\boldsymbol{r}')\phi_{i\sigma}(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}. \tag{38}$$

4.3 Van der Waals dispersion

Dft does not take into account effects caused by charge fluctuations. These Van der Waals effects can be taken care of with different methods. The most straight forward way is simply to add a special non-local functional (VdW-DF method). A similar

approach is to use highly parameterized functionals, like metahybrid functionals (called DFs). Another way is to add dispersion-corrected atom-centered potentials (DCACPs). Recently, the most promising seems to be DFT-D method [6], which is just a sum of terms CR^{-6} over all atom pairs. As it is generally known, for large distances Van der Waals potential should decay as R^{-6}. It is obvious that DFT-D does obey this rule as also does VdW-DF method. The other two unfortunately do not obey it. As a consequence DF and DCACP usually cause underbinding.

4.4   All electron dft calculations

All electron dft calculations are 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. Commonly used open source packages are Orca and Nwchem.

4.5   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. Pseudo potentials 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 have to be constructed prior to a given calculation using some other much simpler system. 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.

5   Dft in crystals

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

$$\psi_{n,\boldsymbol{k}}(\boldsymbol{r}) = u_{n,\boldsymbol{k}}(\boldsymbol{r})e^{i\boldsymbol{k}\boldsymbol{r}}; \qquad u_{n,\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{R}) = u_{n,\boldsymbol{k}}(\boldsymbol{r}), \tag{39}$$

where $\boldsymbol{R}$ is a vector is Bravais lattice of a crystal in question. Functions $u_{n,\boldsymbol{k}}$ 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 $r \to 0$ 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 no 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.

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