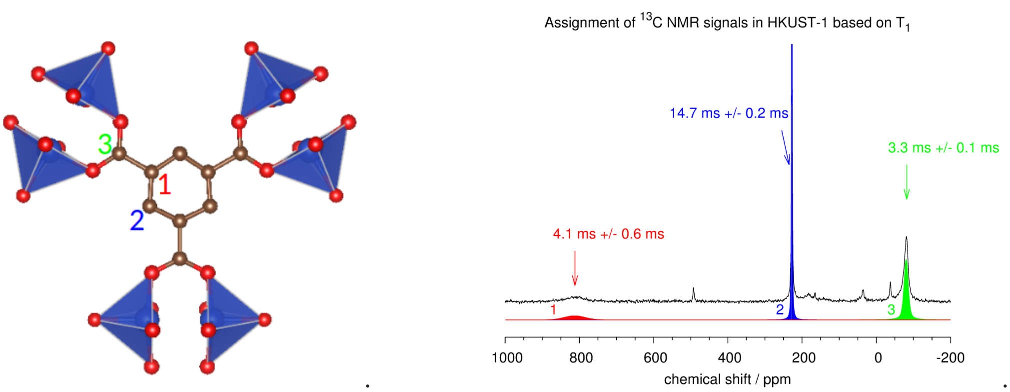
1 Introduction

Metal-organic frameworks or MOFs are materials consisting of one or multiple central metallic ions and surrounding organic ligands. They are crystalline materials with very high porosity. Internal surface area in some cases exceeds 6000 m^2/g [1]. Thanks to their chemical properties they are widely used in the fields of biochemistry, catalysis and electrochemistry. They are especially useful in clean energy applications, as storage for gasses (eg. hydrogen) or energy through adsorption / desorption process [1]. They can also be used as gas separation medium, as second harmonic generators in nonlinear optics, some of them also display interesting ferroelectric properties. Their usage is so broad thanks to numerous combinations of metallic ions and organic ligands [1, 2]. Many MOFs contain unpaired electrons. Ions such as Cu(II), Ni(II) have unpaired electron(s) in their d orbitals and one can clearly see their effects on ^{13}C and ^{1}H NMR spectra, one of the most common tools for characterization of the molecular and electronic structure of organic molecules.

Materials presented in this work are paramagnetic. This means they exhibit weak attraction to the external magnetic field, which is a consequence of unpaired electrons in their structure. The effects of the latter are easily recognized in NMR spectra by the large paramagnetic shifts they cause [3]. Picture 1 shows a spectre of MOF called HKUST-1. One can observe a large shift at around 800 ppm caused by unpaired electrons in molecule.

NMR spectra of organic materials usually feature chemical shifts caused by induced currents which in turn, are caused by external magnetic field [4]. In paramagnetic materials, this is not the only contribution to the total shifts visible in spectra. An important interaction, not present in diamagnetic materials, is interaction between unpaired electrons and nuclei [3]. Such interaction can cause large paramagnetic shifts also called hyperfine shifts. Typical for such spectra are also widened spectral lines. These large shifts make interpretation of spectra more difficult [3]. A useful tool to help with the interpretation are first-principle quantum calculations. Large growth of computational power in recent years have enabled more accurate calculations and calculations performed on a more complex systems.



(a) (b)

Figure 1: An example of MOF named HKUST-1. It is a crystalline material. Image (a) depicts a part of the crystaline structure which is used for calculation of NMR parameters of atoms marked with 1, 2 and 3. (b) ^{13}C-NMR spectra of atoms marked on scheme (a).

Development of computational tools have also enabled computations of shielding and hyperfine tensors. The former is responsible for large shifts caused by unpaired electrons whereas the latter is present in all molecules and is caused by currents induced by external magentic field. Although most common computational packages offer computations of these two tensors, total chemical shifts for paramagnetic materials / MOFs have not yet been systematically tested and documented in the literature.

2 Calculation of electronic wavefunction

Accurate calculation of electronic structure has always been a challenge. It quickly became apparent that direct use of Schrödinger equation is not a realistic prospect, except for some small molecules, as the time consumed to solve it grows exponentially [5] as a function of electron number at a given accuracy level. With the development of computers, different numerical approximations for computation of electronic wave function 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 [5]. Through the years DFT has evolved and today it represents one of the main tools for calculation of electronic structure especially for complex molecules and crystals.

2.1 Hamiltonian

The first step in formulation of the problem is to define hamiltonian which describes the 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 a system is given by the solution of the time independent Schrödinger equation:

$$\hat{H} \left|\psi_0\right\rangle = \epsilon_0 \left|\psi_0\right\rangle, \tag{2}$$

where index 0 denotes the solution with the lowest energy. In general ψ_0 depends on $3N$ coordinates, where N is the total number of particles. This means that systems with more than e.g. 10 atoms are very computationally demanding. It is common practice to reduce the dimensionality of the problem by employing Born-Oppenheimer approximation in which the motion of nuclei is separated from the motion of electrons, sometimes their positions are even fixed [5, 6]. 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 [7]. As one can imagine, solving a system of coupled differential equations with so large number of coordinates ($3N$) is computationally an almost impossible task. This is the reason for development of approaches which, while still being sufficiently accurate, offer shorter computational times. DFT represents one of the most successful methods for solving such systems.

2.2 Density functional theory - DFT

DFT allows us to replaces all electron wave function with electron density and effectively reduce the problem to a single electron problem. The core of DFT lies in Kohn-Sham theorems. These two theorems prove that stationary many-electron systems are fully characterized by their ground state electron density. This means that given a group of electrons, one only has to know ground state electron density to be able to tell all the other properties of this group of electrons [5]. For non-degenerate cases, the latter is uniquely determined by the ground state many-electron wave function, which in turn is uniquely determined by the external potential. Uniquely determined means that there exists bijection between the set of potentials, which yield non-degenerate ground states, the set of ground state wave functions and ground state electron densities. The bijection is depicted on the figure 2. The figure denotes mentioned sets as $\mathcal{V}$, $\mathcal{G}$ and $\mathcal{N}$.

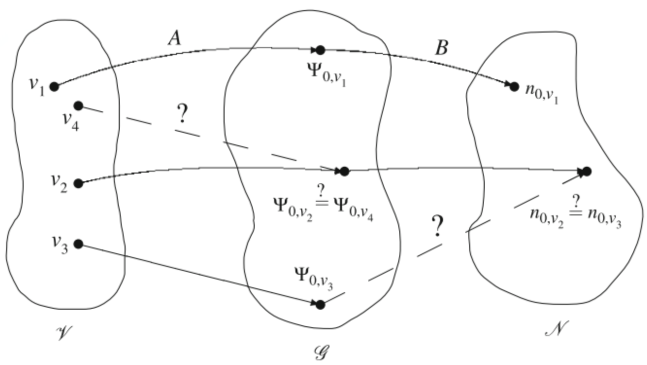


Figure 2: Bijection between the set of potentials, the set of their corresponding ground states and the set of ground state densities. Existance of such bijection is proven by Kohn-Sham theorems and ensures that many-particle system is uniquely determined by its ground state particle density [6].

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 electron density:

$$|\psi_0'\rangle = |\Psi[n_0']\rangle \tag{4}$$

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 electron density:

$$E[n_0] = \langle\Psi[n_0]|\, \hat{H}\, |\Psi[n_0]\rangle\,, \tag{5}$$

for which one can find minimum energy principle: $E[n_0] < E[n]$ whenever $n(\boldsymbol{r})$ 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 $\mathcal{N}$. 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 $\mathcal{N}$ has a corresponding potential V_{ext} such that it minimizes energy functional of the form 5 and consequently they are called V-representable densities. In practice, this is not really important. The reason for this is the discretization of space into grid points. On final grid for any strictly positive electron density ($n(\boldsymbol{r}) > 0$) belongs to $\mathcal{N}$ [6].

3 DFT in practice

Kohn-Sham theorems unfortunately tell nothing about the explicit dependence of energy functional on density. Nonetheless, we would still like to use Kohn-Sham theorems, to construct numerical scheme in which electron density has the central role. From now on will concentrate on construction of a suitable DFT scheme and finding energy functional $E[n(\boldsymbol{r})]$, which should approximate the given system as well as possible.

3.1 Kohn-Sham equations

Kohn-Sham (KS) equations represent a standard and most common approach to DFT. They are based on energy functional dependent only on electron density $n(\boldsymbol{r})$. To introduce them in an understandable and consistent fashion, let's start with a non-interacting system.

3.2 Noninteracting system

Hamiltonian of N-electron non-interacting system can be written in the following way:

$$\hat{H} = \hat{T} + \hat{V}_{ext}, \tag{6}$$

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

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

which, when inserted into equation (6) effectively produces a set of single electron problems:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}_{ext}(\boldsymbol{r})\right)\phi_i(\boldsymbol{r}) = \epsilon_i\phi_i(\boldsymbol{r}). \tag{7}$$

Thus, using slater determinant, we have effectively converted many electron problem with $3N$ coordinates to a single electron problem. Of course the electrons in this case do not feel each other and motion of each electron should not depend on other electrons, so such a breakdown is completely natural (except for Pauli principle, which is already built into the Slater determinant).

The ground state of such a system is obtained by putting pairs of electrons into each of $N/2$ lowest states. Calculation of kinetic energy and electron density for such a system is 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 electron density calculation. Electron density corresponding to such a wave function can be written using the following expression:

$$n_0(\boldsymbol{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_i \Theta(\epsilon_F - \epsilon_i) |\phi_i(\boldsymbol{r}, \sigma)|^2, \tag{8}$$

where Θ is a Heavyside function. The density of electrons is just a sum over all occupied orbitals. Now let's remember Kohn-Sham theorems, which state that ground state density is unique functional of the ground state wave function:

$$|\psi(\boldsymbol{r})\rangle = |\Psi[n(\boldsymbol{r})]\rangle \,. \tag{9}$$

One can show that there exists an even stronger connection; every ϕ_i is a uniquely determined by ground state density. One can see this by considering a single electron problem using the same potential V_{ext} as found in eq. (6) and then gradually adding electrons, thus:

$$|\phi_i(\boldsymbol{r})\rangle = |\Phi_i[n(\boldsymbol{r})]\rangle \,. \tag{10}$$

Using this relations we can define HK functional:

$$E_s[n(\boldsymbol{r})] = \langle \Psi[n(\boldsymbol{r})] | \, T \, |\Psi(n(\boldsymbol{r}))\rangle + \int n(\boldsymbol{r}) V_{ext}(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}, \tag{11}$$

where

$$T[n(\boldsymbol{r})] = \sum_i \Theta(\epsilon_F - \epsilon_i) \sum_{\sigma=\uparrow,\downarrow} \int \phi^*_\sigma(\boldsymbol{r}) \frac{-i\hbar\nabla^2}{2m} \phi_\sigma(\boldsymbol{r}), \tag{12}$$

where we have implicitly used $|\phi_i(\boldsymbol{r})\rangle = |\Phi_i[n(\boldsymbol{r})]\rangle$. In practice this in not necessary, since functions $\phi(\boldsymbol{r})$ are known.

Now we would like to use a similar construction to solve hamiltonian 5. Using solution ansatz in the form of Slater determinant offers straight forward calculation of kinetic energy and electron density. Using Slater determinant leads to differential equations for ϕ_k wavefunctions. Modern computational packages instead of solving differential equations use large sets of basis functions, which in the end lead to an eigenvalue problem. Solution is then given by populating lowest energy orbitals until all electrons are allocated.

To solve interacting system using DFT one relies on the fact, that for every interacting hamiltonian with ground state density n_0, there exists noninteracting hamilotnian with exactly the same ground state density [6]. This fact still does not tell us what kind of external potential one should use to produce the same electron density.

Intuitively, one would expect that potential belonging to effective single electron hamiltonian should reflect the properties, geometry and potentials found in a given interacting system. Hamiltonian naturally contains kinetic energy term, but it should also somehow contain inter particle interactions. Usually Kohn-Sham hamiltonian consists of kinetic energy term, Hartree inter particle interaction, external potential and exchange-correlation functional [6]:

$$E[n(\boldsymbol{r})] = T[n(\boldsymbol{r})] + E_H[n(\boldsymbol{r})] + E_{ext}[n(\boldsymbol{r})] + E_{xc}[n(\boldsymbol{r})]. \tag{13}$$

Hartree term accounts for Coulomb repulsion:

$$E_H[n(\boldsymbol{r})] = \int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}'\mathrm{d}\boldsymbol{r}. \tag{14}$$

The above expression is not the same as the one we get from Hartree-Fock equations and includes self-repulsion. DFT treats exchange term, also arising from Coluomb potential, separately. Computational packages often employ different approximation and optimizations for shorter calculation of this term [8]. Functional belonging to external potential is well known:

$$E_{ext}[n(\boldsymbol{r})] = \int n(\boldsymbol{r})V_{ext}(\boldsymbol{r})\mathrm{d}\boldsymbol{r}. \tag{15}$$

Unfortunately exchange-correlation functional is much less well known. It is defined by the equation (13) and contains all the inter-particle interactions not contained in $T[n(\boldsymbol{r})]$ and $E_H[n(\boldsymbol{r})]$. It is common to divide $E_{xc}[n(\boldsymbol{r})]$ into exchange $E_x[n(\boldsymbol{r})]$ and correlation $E_c[n(\boldsymbol{r})]$ part. The former is defined in such a way that Hartree-Fock ground state density and energy are reproduced, if correlation part is neglected. This is achieved if exchange part of functional has exactly the opposite contribution as excessive hartree term in KS equations:

$$E_x[n(\boldsymbol{r})] = -\frac{1}{2}\sum_{k,l}\Theta(\epsilon_F - \epsilon_k)\Theta(\epsilon_F - \epsilon_l)\int \mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r'}\phi_k^*(\boldsymbol{r},\sigma)\phi_l(\boldsymbol{r},\sigma)w(\boldsymbol{r},\boldsymbol{r'})\phi_l^*(\boldsymbol{r'},\sigma')\phi_k(\boldsymbol{r'},\sigma') \tag{16}$$

The most important contribution of $E_x[n(\boldsymbol{r})]$ is cancellation of self-repulsion. This term is commonly called exact exchange and is not always used in DFT calculations. Exchange functionals based only on electron density are often employed and they do not manage to completely cancel self-repulsion terms. We will take a closer look at them in the following chapter. Correlation term is more difficult to derive and we will not dwell deeper into it. Instead let's have a look at how KS equations are actually solved.

Our goal is to minimize energy of the form (13) using Slater determinant as ansatz for many electron system and density calculation. By considering (15) and (12) one can write KS equation:

$$\left(\hat{T} + V_{ext} + E_H[n(\boldsymbol{r})] + E_{xc}[n(\boldsymbol{r})]\right)|\phi\rangle_i = \epsilon_i |\phi_i\rangle, \tag{17}$$

where density $n(\boldsymbol{r})$ has to be calculated according to equation (8). They are usually determined by inserting ansatz in the form of gaussian basis functions from which one can then construct correct single electron states. Multiplying equation by $\langle\phi|_j$ from the left side yields generalized eigenvalue problem:

$$\langle\phi_j|\left(\hat{T} + V_{ext}(\boldsymbol{r}) + E_H[n(\boldsymbol{r})] + E_{xc}[n(\boldsymbol{r})]\right)|\phi_i\rangle = \epsilon_i\langle\phi_j|\phi_i\rangle. \tag{18}$$

System obviously has to be solved in a self consistent fashion (fig. 3). One starts with the positioning of nuclei into desired positions and construction of nuclei potentials. In parallel with the last step starting electron orbitals $\phi_i^{(0)}$ are constructed. Usually they are written as a series of Gaussian functions. Electron density n^0 can

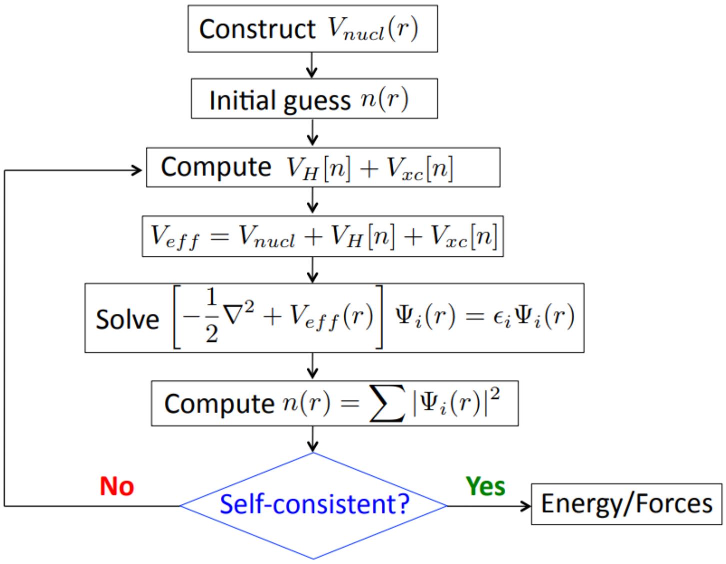


Figure 3: Self consistent scheme depicting the procedure in which Kohn Sham equations are solved. One starts with the positioning of nuclei into desired positions. The next step is to construct potential of nuclei and in parallel one can also construct starting approximation for electronic wave function. The latter is then used for constructing all other functionals of density. After all functionals have been established one can solve KS equations, construct new density and repeat the described procedure until the change in density is not small enough [9].

then be quickly calculated from constructed orbitals. After that one calculates functionals $E_H[n(\boldsymbol{r})]$ and $E_{xc}[n(\boldsymbol{r})]$. In the next step equations are solved. The solution are new orbitals $\phi_i^{(1)}$ and from them, the new density $n^{(1)}$ is calculated. The latter is then used to construct new $E_H[n(\boldsymbol{r})]$ and $E_{xc}[n(\boldsymbol{r})]$ which are again used to solve KS equation from which one gets new orbitals $\phi_i^{(2)}$. The procedure is repeated until the change in density or energy is small enough.

When given a certain system, functionals T, E_H and V_{ext} are precisely determined. E_{xc} is not. It is thus the determining factor for how well the KS equations describe our system. We will present various functionals used today in one of the next chapters.

3.2.1 Degenerate ground state

So far we have talked little about the problem of degeneracy of KS states. In general degeneracy is not a problem, except at Fermi level. When there are more KS states than there are electrons, several possible ground states and thus also electron densities can be constructed. In such cases density matrix arising from several Slater determinants is constructed [6]:

$$\hat{D} = \sum_i d_i \left|\Phi_i\right\rangle \left\langle\Phi_i\right| . \tag{19}$$

Density belonging to such ground state is just a weighted sum of densities corresponding to each Slater determinant $n(\boldsymbol{r}) = \sum_i d_i n_i(\boldsymbol{r})$, where $n_i(\boldsymbol{r}) = \sum_j |\phi_{ij}(\boldsymbol{r})|^2$. Index i runs over all possible Slater determinants one can construct from given degenerate states and index j runs over all states in each Slater determinant. The sum of coefficients d_k is the trace of density matrix and has to be 1. The choice of coefficients d_k is not trivial. They have to be constructed in such a way that the new electron density does not break degeneracy. When a new degenerate state emerges in scf procedure (fig. 3), it may significantly affect electron density and resulting potentials and consequently break or destroy convergence of the procedure. An example is a boron atom where 2p orbitals are degenerate. Only the choice of $d_{2p^0} = d_{2p^{-1}} = d_{2p^1} = 1/3$ leads to spherically symmetric potential and preservation of degeneracy[6].

3.3 Exchange and correlation functionals

Exchange and correlation functionals are functionals which try to account for exchange and correlation interactions between electrons. They can be of different forms and in general one can roughly divide them into four groups [10, 11]: Lda, Gga, meta-Gga and Hybrid functionals. The first three groups all have in common that they explicitly depend on density of electrons. This causes a self-interaction error, which causes excessive delocalization of electrons. As a solution to these problems hybrid functionals, which contain exact Hartree-Fock exchange, have been proposed.

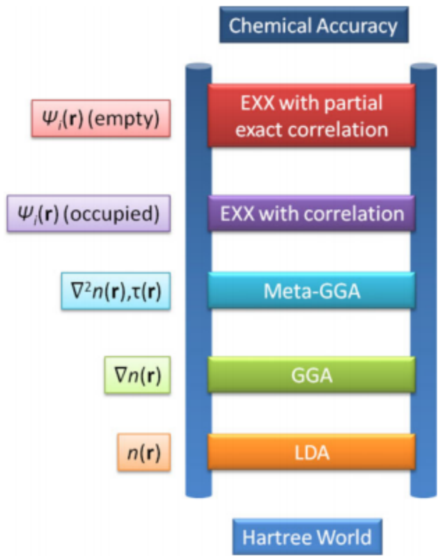


Figure 4: Jacob's ladder of exchange-correlation functional approximations employed in DFT calculations. Hartree world represents starting level where only weak interparticle interaction is present. Lda approxiamtion covers functionals which depend only on electron density. Gga additionally depends on gradient of electron density, while mega-gga incorporates higher order derivatives of electron 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 [12].

3.3.1 Lda

Local density approximation (lda) are functionals which depend only on electron density [10, 11]. First functional of such form dates back into the year 1930, when the exchange interaction for uniform gas was discovered [10] :

$$E_{xc}^{lda}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n(\boldsymbol{r})^{4/3}\mathrm{d}\boldsymbol{r}. \tag{20}$$

The correlation part has not been derived, but it is accurately known from Monte Carlo simulations [11]. Today, there exist multiple other lda exchange–correlation functionals, but for most cases they are not very useful. Their only advantage are short computational times. For every other purpose gga and hybrid functionals are much better suited.

3.3.2 Gga

Generalized gradient approximation (gga) functionals depend not only on electron density, but also on its gradient [10]. Most commonly, gga functionals are built upon (20) [10]:

$$E_{xc}^{gga} = \int n(\boldsymbol{r})^{4/3}F(x); \quad x = |\nabla n(\boldsymbol{r})|/n(\boldsymbol{r})^{4/3}. \tag{21}$$

One of most commonly used gga functionals is PBE functional [10]:

$$E_{xc}^{pbe} = -\int n(\boldsymbol{r})^{4/3}\left[\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} + \frac{\mu s}{1+\mu s^2/\kappa}\right]; \quad s = x/(2(3\pi/2)^{1/3}). \tag{22}$$

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

3.3.3 Meta-gga functionals

Since gga functionals have their short commings, meta-gga functionals were formed in belief that adding higher derivatives will improve accuracy [10]. Meta-gga functionals are built upon gga functional form and add terms containing higher order derivatives of electron density. They higher computational cost than gga functionals, but are not significantly better than gga functionals and are thus not so popular.

3.3.4 Hybrid functionals

On the contrary to meta-gga functionals, hybrid functionals are much more successful [10]. These functionals are not a continuation of lda, gga, meta-gga chain. Instead, they incorporate exact Hartree-Fock exchange term [10]:

$$E_{xc}^{hf} = \sum_{i,j,\sigma}\int \frac{\phi_{i\sigma}^*(\boldsymbol{r})\phi_{j\sigma}(\boldsymbol{r})\phi_{j\sigma}^*(\boldsymbol{r}')\phi_{i\sigma}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{r}'. \tag{23}$$

Such functionals do not break Kohn Sham formalism since the wave functions $\phi_i(\boldsymbol{r})$ are unique functional of densities as shown in previous chapter.

3.4 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 promising seems to be the so called DFT-D method [13], 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} and this interaction does fulfill this condition.

4 NMR measurements

NMR is a technique, where one uses external magnetic field to split the energy levels of a nuclei with a nonzero spin. However, the magnetic field does not affect only the nuclei, but is also affects electrons. Differences in electronic structure is what causes differences among spectra of the same element in different molecules. Thus, using NMR, one can get the information about the environment of the observed nucleus and electronic structure of molecule.

The standard way to measure effects of NMR parameters is to introduce shielding tensor. A unique shielding tensor belongs to each core in a molecule. The tensor depends only on electron density at given nucleus and has non zero values for all nuclei featuring nonzero spin. It contains information about the currents induced by external magnetic fields. It defined by the following equation:

$$\boldsymbol{B}_{eff} = \boldsymbol{B}_{ext}(I - \underline{\underline{\sigma}}). \tag{24}$$

The tensor is not measured directly, instead one measures just a relative deviation from some reference molecule called chemical shift:

$$\underline{\underline{\delta}} = (\underline{\underline{\sigma}}_{ref} - \underline{\underline{\sigma}}_{sample})(I - \underline{\underline{\sigma}}_{ref})^{-1} \to \delta^{iso} \approx \sigma^{iso}_{ref} - \sigma^{iso}_{sample}. \tag{25}$$

The left part of equation is the rigorous definition. More commonly, the right part is used, which is a trace of the left side under the assumption that $(\underline{\underline{\sigma}}_{ref})_{ij} \ll 1$. The latter is basically always true. . The other important tensor is hyperfine shielding tensor. It describes magnetic (spin—spin) interaction between unpaired electrons and given nucleus.

There are two contributions to the shielding tensor - paramagnetic and diamagnetic. The former is only present in materials with unpaired electrons and should not be confused with hyperfine tensor, also present in such materials. Diamagnetic contribution can be, in the first order of perturbation, calculated as [4]:

$$\sigma^{d}_{\alpha\beta} = \langle\psi_0| \boldsymbol{r}_k \boldsymbol{r}_{Nk} \delta_{\alpha\beta} - \boldsymbol{r}_k \boldsymbol{r}_{Nk} |\psi_0\rangle \tag{26}$$

and a similar expression holds also for paramagnetic contribution $\sigma^{p}_{\alpha\beta}$. Both expressions are nonlinear in $\boldsymbol{r}$. This seems to suggest that the values depend on the origin. It turns out, that the sum of both contributions does not depend on the origin, but only when one uses complete set of basis functions, which, in practice, is almost never the case. This is a serious problem because the terms that should theoretically cancel out have nontrivial contribution [4]. The issue is exaggerated by the fact that diamagnetic and paramagnetic contributions are of a different perturbation order.

In contrast to shielding tensor, which depends only on electron density, hyperfine tensor depends on spin density [14]. The anisotropic part of the tensor, also called Fermi contact term, is calculated as follows:

$$A_{iso} = \frac{4\pi}{6c^2} g_e g_N \beta_N \langle S_z \rangle \rho^{beta-alpha}(0), \tag{27}$$

where g_e and g_n are electronic and nuclear g-factors, $\langle S_z \rangle$ is the expectation value of z component of total spin. $\rho^{beta-alpha}$ is the difference between spin up and spin down electron densities. Fermi contact term stems from magnetic dipole interaction between unpaired electron and nucleus. Dipole dipole interaction also has anisotropic contribution to tensor, which is called dipolar term. Higher order contributions are caused by the relativistic effects. Relative sizes of hyperfine and chemical shifts vary greatly depending on electronic configuration of molecule, however, hyperfine shifts can reach much larger values than chemical shifts.

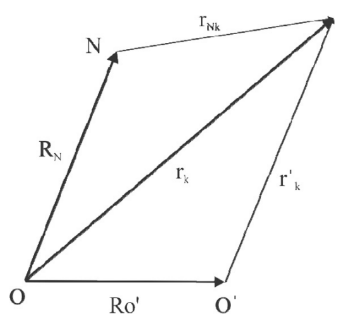


Figure 5: Translation of the coordinate system for vector $\boldsymbol{Ro'}$. $\boldsymbol{R_N}$ points to N-th atom, whereas small case $\boldsymbol{r}$ point to electrons [4].

5 Purpose

The purpose of this work and the follow on work associated with phd thesis, is to systematically test various approaches and computational packages. Since MOFs are crystalline materials one can choose periodic boundary conditions. The other options is to use large cut-out of crystal structure and non-periodic boundary conditions to calculate electronic structure. In the latter case one need to add atoms at the boundaries, so that one does not end up with radicals. Of course, the former approach also has downsides. These are mainly associated with the use of plane waves as basis sets and their inability to fit steep, multi nodal, high angular momentum states of d shell electrons. For the same reason, the inner electrons are often replaced by pseudo wave function, also called pseudopotential. Although pseudopotentials are carefully constructed, they still represent an approximation which may yield significant inaccuracies.

The other source of inaccuracies is the DFT method itself. Depending on exchange—correlation functional used, one may obtain very different results. The self interaction error of common dft poses a significant error especially for metals, where valence electrons get over delocalized, causing large error in electron density and thus also NMR parameters. To conclude this seminar, we are attaching examples of two MOFs, for which NMR parameters were measured and calculated. One is already discussed HKUST-1 and the other consists of central copper ion and two molecules of acetil—acetonat.

$Cu - (acetilacetonat)_2$					
	QE: PBE		ORCA: PBE0		
C	δ^{cs}	δ^{tot}	σ^{cs}	δ^{tot}	eks.
4	118	59	109	80	108
6	37	270	30	199	-53
10	209	199	196	186	97

Table 1: This is an example of a molecule where calculations differ significantly from experiments. Using two different computational packages and two completely different approaches yields quite similar results, but unfortunately both are quite far from the measurements.

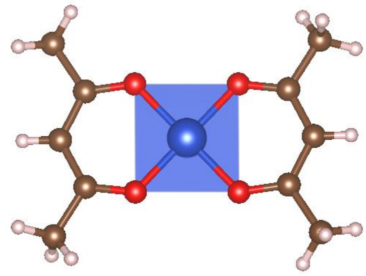


Figure 6: A molecule of $Cu - (acetilacetonat)_2$.

HKUST - 1							
	PBE		PBE0		TPSS0		
C	δ^{cs}	δ^{tot}	δ^{cs}	δ^{tot}	δ^{cs}	δ^{tot}	eks.
36	178	-171.3	175	-76.5	171	-81.2	-50
37	140	1028.4	134	802.7	130	798.2	853
38	138	299.8	138	218.6	136	216.6	228

Table 2: HKUST-1 calculation data compared to experimental values. The values are quite close for both hybrid functionals - PBE0 and TPSS0. Gga fucntional PBE fared much worse.

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