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Thesis topic defense seminar

Calculation of nmr parameters in paramagnetic metallo-organic materials

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1 Introduction

Metallo-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 $6000 \text{ m}^2/\text{g}$ [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 ^1H 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].

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. Development of computational tools have also enabled computations of shielding and hyperfine tensors. The former is responsible for large shifts caused by unpaired elec-

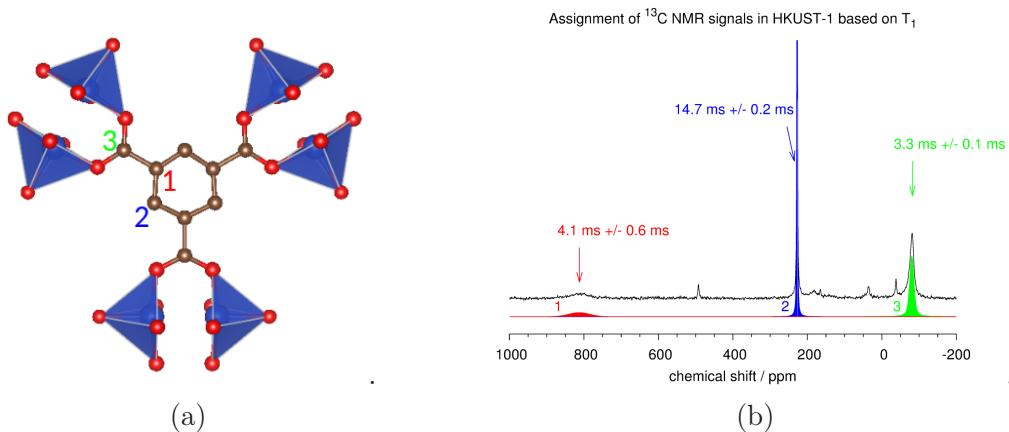


Figure 1: An example of MOF named HKUST-1. It is a crystalline material. Image (a) depicts a part of the crystalline structure which is used for calculation of nmr parameters of atoms marked with 1, 2 and 3. (b) ^{13}C -nmr spectra of atoms marked on scheme (a).

trons whereas the latter is present in all molecules and is caused by currents induced by external magnetic 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 literature.

In this work we will present the most common approach to calculation of nmr parameters of paramagnetic materials, which is based on density functional theory (DFT). First we will present basics of DFT, which is the most important part of the whole procedure. Values of nmr parameters completely depend on electronic configuration, consequently it's accurate calculation is of a paramount importance.

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:

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

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

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

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 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:

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

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 [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 replace 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. For a simple non-degenerate case we will prove these two theorems. 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 inter-particle interaction and V_{ext} is external potential determined up to a constant. Let V_{ext} be such a potential that ground state ψ_0 is non-degenerate. Consider now the set of all H of the form (4), which differ only in the V_{ext} , with non-degenerate ground states. Since kinetic and inter-particle interaction terms are the same for all H in such a set, the latter can be represented by the set of all non-equivalent potentials:

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

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

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

The map from \mathcal{V} to \mathcal{G} is surjective by definition. What we would like to know is, if it is also injective (4), 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:

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

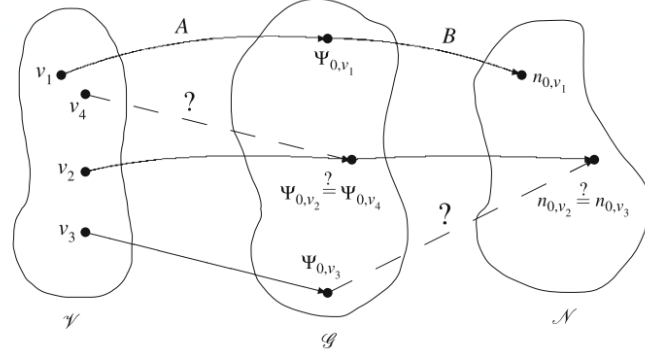


Figure 2: Bijection between the set of potentials, the set of their corresponding ground states and the set of ground state densities. Existence of such bijection is proven by Kohn-Sham theorems and ensures that many-particle system is uniquely determined by its ground state particle density [6].

which is a contradiction, since V_{ext} and V'_{ext} must 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 densities, which are supposed to be the same for both wave functions:

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

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

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

and

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

Where $n(\mathbf{r})$ is density corresponding to $|\psi\rangle_0$ and $|\psi'\rangle'_0$. 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 electron density. Ground state electron densities form a set where each density corresponds to a single wave function from \mathcal{G} :

$$\mathcal{N} = \{n; n = \langle \psi_0 | \hat{n} | \psi_0 \rangle, \psi_0 \in \mathcal{G}\}, \quad (15)$$

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

Extension of this simple proof 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 with magnetic fields, where one can separate hamiltonian into spin up and spin down

hamiltonian of the form (4). In the latter case one obtains bijections between the set of pairs $(\mathbf{A}(\mathbf{r}), V_{ext}(\mathbf{r}))$, $(\psi_{\uparrow}, \psi_{\downarrow})$ and $(n(\mathbf{r}), \mathbf{m}(\mathbf{r}))$.

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 electron density:

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

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 electron density:

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

for which one can find minimum energy principle: $E[n_0] < E[n]$ whenever $n(\mathbf{r})$ 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 nonnegative normalizable function $n(\mathbf{r})$ 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 17 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 ($n(\mathbf{r}) > 0$) 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 $E[n(\mathbf{r})]$, 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 $n(\mathbf{r})$. 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:

$$\hat{H} = \hat{T} + \hat{V}_{ext}, \quad (18)$$

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:

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

which, when inserted into equation (18) effectively produces a set of single electron problem:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + \hat{V}_{ext}(\mathbf{r}) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}). \quad (19)$$

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 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:

$$n_0(\mathbf{r}) = \sum_{\sigma=\uparrow, \downarrow} \sum_i \Theta(\epsilon_F - \epsilon_i) |\phi_i(\mathbf{r}, \sigma)|^2. \quad (20)$$

, 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:

$$|\psi(\mathbf{r})\rangle = |\Psi[n(\mathbf{r})]\rangle. \quad (21)$$

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. (18) and then gradually adding electrons, thus:

$$|\phi_i(\mathbf{r})\rangle = |\Phi_i[n(\mathbf{r})]\rangle. \quad (22)$$

Using this relations we can define HK functional:

$$E_s[n(\mathbf{r})] = \langle \Psi[n(\mathbf{r})] | T | \Psi[n(\mathbf{r})] \rangle + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}, \quad (23)$$

where

$$T[n(\mathbf{r})] = \sum_i \Theta(\epsilon_F - \epsilon_i) \sum_{\sigma=\uparrow, \downarrow} \int \phi_\sigma^*(\mathbf{r}) \frac{-i\hbar \nabla^2}{2m} \phi_\sigma(\mathbf{r}), \quad (24)$$

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

Now we would like to use a similar construction to solve hamiltonian 17. 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 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 hamiltonian 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]:

$$E[n(\mathbf{r})] = T[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{ext}[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})]. \quad (25)$$

Hartree term accounts for Coulomb repulsion:

$$E_H[n(\mathbf{r})] = \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}, \mathbf{r}'|} d\mathbf{r}' d\mathbf{r}. \quad (26)$$

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 Coulomb 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:

$$E_{ext}[n(\mathbf{r})] = \int n(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r}. \quad (27)$$

Unfortunately exchange-correlation functional is much less well known. It is defined by the equation (25) and contains all the inter-particle interactions not contained in $T[n(\mathbf{r})]$ and $E_H[n(\mathbf{r})]$. It is common to divide $E_{xc}[n(\mathbf{r})]$ into exchange $E_x[n(\mathbf{r})]$ and correlation $E_c[n(\mathbf{r})]$ 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:

$$E_x[n(\mathbf{r})] = -\frac{1}{2} \sum_{k,l} \Theta(\epsilon_F - \epsilon_k) \Theta(\epsilon_F - \epsilon_l) \int d\mathbf{r} d\mathbf{r}' \phi_k^*(\mathbf{r}, \sigma) \phi_l(\mathbf{r}, \sigma) w(\mathbf{r}, \mathbf{r}') \phi_l^*(\mathbf{r}', \sigma') \phi_k(\mathbf{r}', \sigma') \quad (28)$$

The most important contribution of $E_x[n(\mathbf{r})]$ 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 (25) using Slater determinant as ansatz for many electron system and density calculation. By considering (27) and (24) one can write KS equation:

$$\left(\hat{T} + V_{ext} + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] \right) |\phi\rangle_i = \epsilon_i |\phi\rangle_i, \quad (29)$$

where density $n(\mathbf{r})$ has to be calculated according to equation (20). 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:

$$\langle\phi_j| \left(\hat{T} + V_{ext}(\mathbf{r}) + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})] \right) |\phi_i\rangle = \epsilon_i \langle\phi_j|\phi_i\rangle. \quad (30)$$

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 then be quickly calculated from constructed orbitals. After that one calculates functionals $E_H[n(\mathbf{r})]$ and $E_{xc}[n(\mathbf{r})]$. 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 $E_H[n(\mathbf{r})]$ and $E_{xc}[n(\mathbf{r})]$ which are again used to solve KS equation from which one gets new orbitals $\phi^{(2)}$. 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]:

$$\hat{D} = \sum_i d_i |\Phi_i\rangle \langle\Phi_i|. \quad (31)$$

Density belonging to such ground state is just a weighted sum of densities corresponding to each Slater determinant $n(\mathbf{r}) = \sum_i d_i n_i(\mathbf{r})$, where $n_i(\mathbf{r}) = \sum_j |\phi_{ij}(\mathbf{r})|^2$. 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

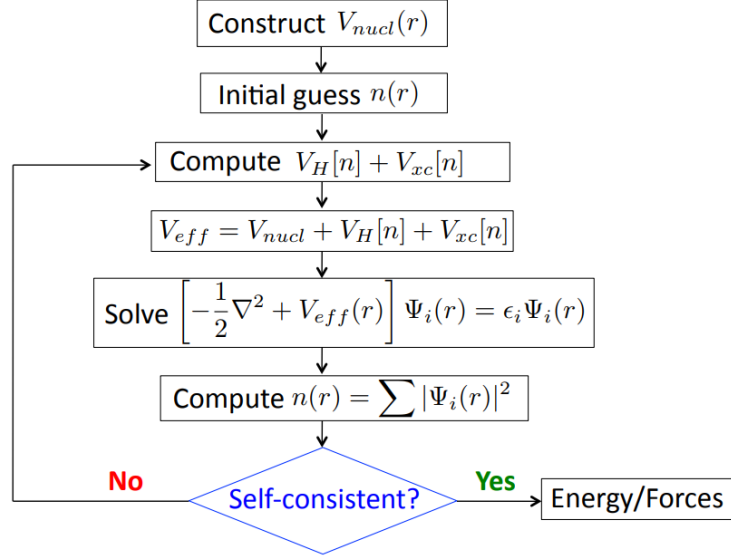


Figure 3: Self consistent scheme depicting the procedure in which Kohn Sham equations are solved. One starts with the positioning of nuclei into desired positions. The next step is to construct potential of nuclei and in parallel one can also construct starting approximation for electronic wave function. 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].

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.

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] :

$$E_{xc}^{lda}[n] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int n(\mathbf{r})^{4/3} d\mathbf{r}. \quad (32)$$

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 (32) [10]:

$$E_{xc}^{gga} = \int n(\mathbf{r})^{4/3} F(x); \quad x = |\nabla n(\mathbf{r})|/n(\mathbf{r})^{4/3}. \quad (33)$$

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

$$E_{xc}^{pbe} = - \int n(\mathbf{r})^{4/3} \left[\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} + \frac{\mu s}{1 + \mu s^2/\kappa} \right]; \quad s = x/(2(3\pi/2)^{1/3}). \quad (34)$$

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 shortcomings, 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. Functionals are formulated according to the following equation [10]:

$$E_{xc}^{MGA} = \int \rho^{4/3} F(\rho(\mathbf{r})\nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau(\mathbf{r})); \quad \tau = \frac{1}{2} \sum_i |\nabla\phi_i(\mathbf{r})|^2 \quad (35)$$

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.

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]:

$$E_{xc}^{hf} = \sum_{i,j,\sigma} \int \frac{\phi_{i\sigma}^*(\mathbf{r})\phi_{j\sigma}(\mathbf{r})\phi_{j\sigma}^*(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \quad (36)$$

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

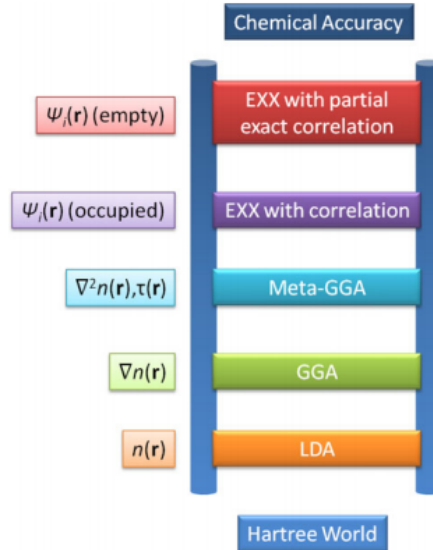


Figure 4: Jacob’s ladder of exchange-correlation functional approximations employed in DFT calculations. Hartree world represents starting level where only weak interparticle interaction is present. Lda approxiamtion covers functionals which depend only on electron density. Gga additionally depends on 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].

3.4 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 All electron vs pseudopotential

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 states 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 the 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.

All electron calculations avoid pseudopotential by taking into account all electrons. The latter does cost some computational time, but depending on the molecule, it may be the only way to get reliable result. Of course, for large molecules all electron calculations are significantly more expensive. Commonly used open source packages offering both approaches are Orca and Nwchem.

5 Nmr parameters

The two most important nmr quantities are shielding tensor and hyperfine tensor. The former is important in all organic materials, while the latter is present only in materials with unpaired electrons. Shielding tensor is proportionate to electron density at the observed core site, whereas hyperfine tensor is proportionate to the shielding tensor.

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]:

$$\sigma_{\alpha\beta}^d = \langle \psi_0 | \mathbf{r}_k \mathbf{r}_{Nk} \delta_{\alpha\beta} - \mathbf{r}_k \mathbf{r}_{Nk} | \psi_0 \rangle \quad (37)$$

and a similar expression holds also for paramagnetic contribution $\sigma_{\alpha\beta}^p$. Both expressions are nonlinear in \mathbf{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 non-trivial 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:

$$A_{iso} = \frac{4\pi}{6c^2} g_e g_N \beta_N \langle S_z \rangle \rho^{\text{beta-alpha}}(0), \quad (38)$$

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. $\rho^{\text{beta-alpha}}$ is the difference between spin up and spin down

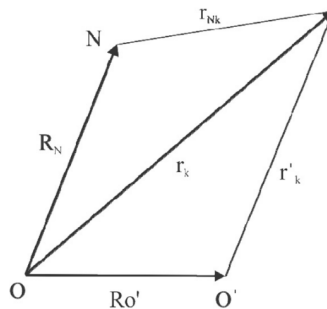


Figure 5: Translation of the coordinate system for vector $\mathbf{R}_{O'}$. \mathbf{R}_N points to N -th atom, whereas small case \mathbf{r} point to electrons [4].

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 spin-orbit coupling and the relativistic dipolar terms. 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.

6 Conclusion

In this paper we tried to provide a clear and comprehensive review of steps needed to calculate nmr parameters. The single most important step is accurate calculation of electronic wave function. The latter is most commonly calculated using DFT, which has been in use for a long time and is still actively evolving. Popular computational packages offer large variety of functionals, which are suitable for numerous systems and their property calculations.

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