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DFTB for studying chemical systems

Author
T. E. Ødegård

Supervisor
T. S. van Erp

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Abstract

In this text the derivations of the Hartree Fock, density function theory and density function based tight binding has been derived, but not post methods. We then look at some of the some of the assumption on the Hartree Fock and density function theory. Density function based tight binding is then looked at as a technique and the application on the technique as well as a rough look at the accuracy.
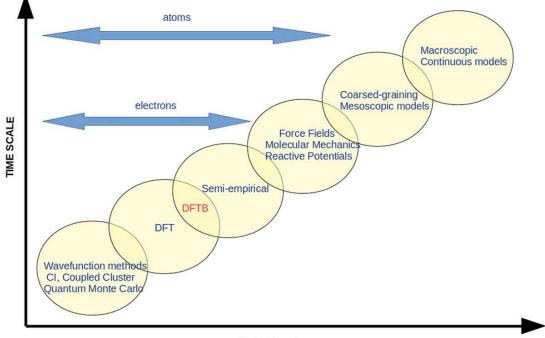
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1 Introduction

Computational chemistry has been a keen part in understanding of how systems of particles is build up and interact with other systems. The way to this point has been long and been through many known names. From the black body radiation to the duality of matter to the Schrödinger equation, in short, the system of particles could be explained. Because of electron-electron repulsion only a few particles be solved exactly and the need to solve numerical was needed. Along this road two different approaches has been arrived, the Hartree-Fock approach with its post Hartree-Fock methods, which uses the wave function, and density function theory (DFT), which uses an electron density.

These system have given a good approximation at describing small particles and systems. However, when it comes to larger particles and systems, like organic chemistry, the calculation can take up long time and computational resources. To be able to compute these systems new approximations need to be made in semi-empirical methods. One of these techniques is density function based tight binding (DFTB), which builds on DFT. Figure 1.1 shows where the DFTB scheme lies compared to other techniques.

Figure 1.1: A size and time scale of simulation methods used in chemistry and material science.[1]

In this paper the derivation Hartree-Fock, DFT and DFTB will be derived. However, they use similar principles which will be derived under the Hartree-Fock approach. Further the use of DFTB will be discussed against DFT and HF to find if DFTB gives accurate results.

2 Theory

2.1 Quantum Theory

2.1.1 The Schrödinger equation

A given system of particles can be explained by the wave function theory. It describes each quantum state of a system using a single function denoted as Ψ. The wave function is depends on the position of the particles and time. Where the positions of electrons is denoted with $\vec{r}_i$

and nucleus with $\vec{R}_i$ and t for time, giving $\Psi(\vec{r}, \vec{R}, t)$. From the Born interpretation we get that the square modulus of the wave function will give the probability of finding a given electron. To get a readable probability the wave function is scaled by a factor N so the sum is equal to 1. The wave function is then normalised, as in the rest of the text, and can be written as

$$\int_{-\infty}^{\infty} |\Psi(\vec{r}, \vec{R}, t)|^2 d\vec{r} = \int_{-\infty}^{\infty} \Psi^*(\vec{r}, \vec{R}, t)\Psi(\vec{r}, \vec{R}, t)d\vec{r} = \langle \Psi(\vec{r}, \vec{R}, t)|\Psi(\vec{r}, \vec{R}, t)\rangle = 1 \qquad (2.1)$$

where the second last equality introduces a compacted notation called the bra-ket notation. The ket, $|\Psi\rangle$, is the regular function and the bra, $\langle\Psi|$, is the complex conjugated function. Combining the bra and ket we get an integral. The wave function is usually orthonormal as well and we get for the wave function the cronical delta

$$\langle \Psi_i|\Psi_j\rangle = \delta_{ij} \begin{cases} i \neq j \implies 0 \\ i = j \implies 1 \end{cases} \qquad (2.2)$$

If the wave function is not orthonormal we get overlap indices denoted S_{ij} which has a value between 0 and 1. Furthermore we introduce observables, an observable is the expected value of an operator (acts on a function on its right), $\hat{\Omega}$, that acts on a ket. A function is called an eigenfunction if it returns itself with an value, ω (eigenvalue), as a multiple.

$$\langle \hat{\Omega}\rangle = \frac{\langle\Psi|\hat{\Omega}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \doteq \omega\langle\Psi|\Psi\rangle = \omega[\Psi] \qquad (2.3)$$

where $\doteq$ is possible given the condition the operator is Hermitian and wave function is normalised. The importance of Hermitian operators is that they always gives real numbers by satisfying $\hat{\Omega} = \hat{\Omega}^\dagger$, and by doing it they can act on the bra or ket ($\langle\Psi|\hat{\Omega}|\Psi\rangle = (\langle\Psi|\hat{\Omega}|\Psi\rangle)^*$). $\omega[\Psi]$ denotes the eigenvalue and can be describes as a functional (function of functions). It can be showed that the potential and kinetic operators to the wave function is Hermitian and by combining these operators we get the Hamiltonian operator $\hat{H}$. The system of the wave function can is described by the Schrödinger equation where

$$\hat{H}\Psi(\vec{r}, \vec{R}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}, \vec{R}, t) \qquad (2.4)$$

By assuming the time and position can be separated, we get the time independent Schrödinger equation

$$\hat{H}\Psi(\vec{r}, \vec{R}) = E\Psi(\vec{r}, \vec{R}) \qquad (2.5)$$

where E is the total energy of the system. The Hamiltonian is composed of the kinetic and potential operators

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{eN} \qquad (2.6)$$

where $\hat{T}_N$ and $\hat{T}_e$ is the total kinetic energy of the nucleus and electrons, $\hat{V}_{NN}$ and $\hat{V}_{ee}$ is the nucleus-nucleus and electron-electron repulsion and $\hat{V}_{eN}$ is the electron-nucleus attraction. These operators can be shown to be

$$\hat{T}_N = -\sum_{I=1}^{N} \frac{1}{2M_I}\nabla_i^2 \qquad (2.7a)$$

$$\hat{T}_e = -\sum_{i=1}^{n} \frac{1}{2} \nabla_i^2 \tag{2.7b}$$

$$\hat{V}_{NN} = \sum_{I=1}^{N} \sum_{J>I}^{N} \frac{Z_I Z_J}{r_{IJ}} \tag{2.7c}$$

$$\hat{V}_{ee} = \sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{r_{ij}} \tag{2.7d}$$

$$\hat{V}_{eN} = -\sum_{i=1}^{n} \sum_{I=1}^{N} \frac{Z_I}{r_{iI}} = \sum_{i=1}^{n} v(\vec{r}_i) \tag{2.7e}$$

where $\nabla = \frac{\partial}{\partial x_1} + \cdots + \frac{\partial}{\partial x_n}$, the partial derivative across all dimensions. M_I is mass ratio and Z_I is the charge ratio of nucleus I compared to an electron and r_{ab} is the distance between particle a and b. $\hat{V}_{eN}$ is also described as the external potential that acts on electron i, denoted $v(\vec{r}_i)$. All of the equations give the Hartree energy which use the atomic units where $E_{Hartree} = \frac{\hbar^2}{m_e a_0^2} = m_e(\frac{e^2}{4\pi\epsilon_0 \hbar})^2$, and will be used for the rest of text. Where $\hbar$ is the reduced Plack constant, m_e is the electron mass, a_0 is the Bohr radius and ϵ_0 is the electric constant.

2.1.2 Born-Oppenheimer approximation

The Schrödinger equation can be solved analytically for the hydrogen atom (to body problem). However, simple molecules cannot be solved analytically. As systems grows the calculations needed grows as well. To simplify the system we use the Born-Oppenheimer approximation which notes the large difference in mass between the electron and the nucleus. We therefore assume that the nucleus are stationary so the wave function can be separated to $\psi_e(\vec{r}; \vec{R})$ and $\psi_N(\vec{R})$ and like wise for the Hamiltonian into a nucleus and an electronic Hamiltonian with H_e being

$$\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN} + \hat{V}_{NN} \tag{2.8}$$

$\hat{V}_{NN}$ is included because it becomes a constant, but can be added at any time of calculations. The nucleus Hamiltonian is the remaining operator $\hat{T}_N$. The Schrödinger equations can then be rewritten into two equations

$$\hat{H}_e(\vec{r}; \vec{R})\psi_e(\vec{r}; \vec{R}) = E_e(\vec{R})\psi_e(\vec{r}; \vec{R}) \tag{2.9a}$$

$$\left(\hat{T}_N(\vec{R}) + E_e(\vec{R})\right)\psi_N(\vec{R}) = E\psi_N(\vec{R}) \tag{2.9b}$$

The system is calculated multiple times over different nucleus configuration and a map/graf of the energies are found and the optimal configuration is found. This approximation is reliable for ground electronic states and less reliable for excited states. The approximation gives a mean to calculate H_2^+ exactly.

2.1.3 Variational principle and Lagrange multiplier

The energy for a system is described by Equation 2.3, however the wave function is not known excact. To work around this we introduce the variational priciple where we guess a trial wave function Ψ_{trial} and find the Rayligth-ratio,

$$\mathscr{E} = \frac{\langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle}{\langle \Psi_{trial} | \Psi_{trial} \rangle} \tag{2.10}$$

where it can be proved that the Rayligth-ratio energy $\mathscr{E}$ is always larger (or equal) than the ground state energy E_0. What this is implies is that we have a way to describe an upper bound of the energy to a system. The trial function can be expressed by a set of basis function

$$\Psi_{trial} = \sum_{i}^{n} c_i \psi_i \tag{2.11}$$

where ψ_i is the basis and c_i is a constant. To minimise the $\langle \hat{H} \rangle$ we introduce the Lagrange multiplier λ under the constraint that $\langle \Psi | \Psi \rangle$ is equal to 1.

$$\mathscr{L}(c_1, ..., c_n, \lambda) = \langle \Psi | \hat{H} | \Psi \rangle - \lambda(\langle \Psi | \Psi \rangle - 1) \tag{2.12}$$

where Ψ can be expressed by Equation 2.11 with the corresponding c values in the $\mathscr{L}$. We then introduce a small change to c values denoted δc and the $\mathscr{L}$ can be expressed as

$$\mathscr{L}(c_1 + \delta c_1, ..., c_n + \delta c_n, \lambda) = \mathscr{L} + \delta \mathscr{L} + \mathcal{O}(\delta c_n^2) \tag{2.13}$$

since δc_i is small, $\mathcal{O}(\delta c_n^2)$ is approximate zero. The $\mathscr{L}$ is the same as in Equation 2.12 and we need to solve for $\delta \mathscr{L} = 0$ in Equation 2.13.

2.1.4   Hartree-Fock and Slater determinants

The wave function Ψ propagates through the 3D space and is called a spatial orbital. However, each particle also has a property called spin, given by the spin functions $\alpha(\omega)$ and $\beta(\omega)$ where ω is the spin coordinate. The new function is denoted as ϕ

$$\phi(\vec{x}) = \begin{cases} \psi(\vec{r})\alpha(\omega) \\ \psi(\vec{r})\beta(\omega) \end{cases} \tag{2.14}$$

and gives us the spin orbitals, where $\vec{x} = \{\vec{r}, \omega\}$ As electrons are fermions, the electrons needs to be treated as indistinguishable and an exchange of two fermions will change the sign of the system, $\psi(\vec{x}_1, ..., \vec{x}_n) = -\psi(\vec{x}_n, ..., \vec{x}_1)$. This is summarised in the anti-symmetry principle and by looking at Equation 2.14 we see that to fulfil this principle there can be no spin orbitals alike. The spatial orbital is split in two different spin orbitals and therefore spatial orbitals can only hold two electrons, this is known as the Pauli principle.

Following the anti-symmetry principle we want to solve Equation 2.9a as the Hartree-Fock approach. Because of $\hat{V}_{ee}$ this equation cannot be solved exact and needs to be approximated, where the simplest approximation is the Hartree product

$$\Psi(\vec{x}_1, \vec{x}_2, ..., \vec{x}_n) = \phi(\vec{x}_1)\phi(\vec{x}_2)\cdots\phi(\vec{x}_n) \tag{2.15}$$

with n electrons. However, the Hartree product does not fulfill the anti-symmetry principle, but this can be fixed by creating an linear combination of different Hartree products which combined can be written as a Slater determinant (SD).

$$\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\vec{x}_1) & \phi_2(\vec{x}_1) & \cdots & \phi_n(\vec{x}_1) \\ \phi_1(\vec{x}_2) & \phi_2(\vec{x}_2) & \cdots & \phi_n(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\vec{x}_n) & \phi_2(\vec{x}_n) & \cdots & \phi_n(\vec{x}_n) \end{vmatrix}. \tag{2.16}$$

where $\frac{1}{\sqrt{n!}}$ is the normalisation factor. The Hartree-Fock approach then minimize the SD using the variational principle.

$$E[\Psi^{\mathrm{SD}}] = \langle \hat{H} \rangle = \left\langle \Psi^{\mathrm{SD}} \left| \hat{H} \right| \Psi^{\mathrm{SD}} \right\rangle = \left\langle \Psi^{\mathrm{SD}} \left| \sum_i^n -\frac{1}{2}\nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} \right| \Psi^{\mathrm{SD}} \right\rangle$$
$$+ \left\langle \Psi^{\mathrm{SD}} \left| \sum_i^n \sum_{j>i}^n \frac{1}{r_{ij}} \right| \Psi^{\mathrm{SD}} \right\rangle = \sum_i^N \langle \phi_i | \hat{h} | \phi_i \rangle + \frac{1}{2} \sum_i^n \sum_j^n \langle \phi_i \phi_j \| \phi_i \phi_j \rangle \tag{2.17}$$

where we split the Hamiltonian into a single electron operator denoted $\hat{h}(i)$, where $(i) \equiv \vec{x}_i$, the core Hamiltonian, and the two electron operator

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - v(i) \tag{2.18a}$$

$$\langle \phi_i(1)\phi_j(2) \| \phi_i(1)\phi_j(2) \rangle = \langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_i(1)\phi_j(2) \rangle - \langle \phi_i(1)\phi_j(2) | \frac{1}{r_{12}} | \phi_j(1)\phi_i(2) \rangle \tag{2.18b}$$

We then use the Lagrangian multipliers under the constraint that the orbitals are orthonormal

$$\mathscr{L}[\Psi^{SD}] = \langle \hat{H} \rangle - \sum_{i,j} \epsilon_{ij}(\langle \phi_i | \phi_j \rangle - \delta_{ij}) \tag{2.19}$$

Because of hermitian matrix $\epsilon_{ij} = \epsilon_{ji}$ and by introducing small change in the orbitals in SD we get the Fock operator $\hat{f}$

$$\hat{f}(1)|\phi_i\rangle = \epsilon_i |\phi_i(1)\rangle \tag{2.20a}$$

which is an eigenvalue for the orthonormal spin orbitals called canonical Hartree-Fock and the sum of these Fock operator is denoted as $\hat{F}$. The Fock operator consist of new operator, the Coulomb operator $\hat{J}_j$ and the exchange operator $\hat{K}_j$ and they are given as

$$\hat{f}(1)|\phi_i(1)\rangle = \left[\hat{h}(1) + \sum_j^n (J_j(1) - K_j(1)) \right] |\phi_i(1)\rangle \tag{2.20b}$$

$$\hat{f}(1)|\psi_i(1)\rangle = \left[\hat{h}(1) + \sum_j^{n/2} (2J_j(1) - K_j(1)) \right] |\psi_i(1)\rangle \tag{2.20c}$$

$$\hat{J}_j(1)|\phi_i(1)\rangle = \langle \phi_j(2) | \frac{1}{r_{12}} | \phi_j(2) \rangle |\phi_i(1)\rangle \tag{2.20d}$$

$$\hat{K}_j(1)|\phi_i(1)\rangle = \langle \phi_j(2) | \frac{1}{r_{12}} | \phi_i(2) \rangle |\phi_j(1)\rangle \tag{2.20e}$$

The sum of the two electron operator in Equation 2.20b gives an average potential energy of electron 1 due to the presence of the n - 1 other electrons. The same applies for Equation 2.20c, however this is for a closed shell system where the spatial orbitals are filled and the spin is integrated out, called the restricted Hartree-Fock (RHF). For RHF the Fock operator acts on a n/2 set of spatial orbitals that we expand to a set of G known spatial orbitals, mainly atomic orbitals, as

$$\psi_i = \sum_{g=1}^G C_{ig}\chi_g \tag{2.21}$$

The system can then be solved using the Roothaan-Hall equations

$$\mathbf{F(C)C} = \mathbf{SC}\epsilon \tag{2.22}$$

where all are GxG matrixses and S is the overlap matrix explained with Equation 2.2, and the equation is solved iterative based on the values of $\mathbf{C}$. The energy of this RHF system, can be shown to be

$$E_{\text{HF}} = 2\sum_i \langle\psi_i|\hat{h}|\psi_i\rangle + \sum_i \sum_j 2\langle\psi_i\psi_j|\frac{1}{r_{12}}|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\frac{1}{r_{12}}|\psi_j\psi_i\rangle \tag{2.23}$$

2.1.5 Energy correlation

The energy found from the Hartree Fock method has an energy correlation E_{Corr} which can be summarised as

$$E_{Corr} = E_{Exact} - E_{HF} \tag{2.24}$$

where E_{Exact} is the exact energy of the system and E_{HF} is the calculated energy. Since the Hartree-Fock methode is variational, the energy correlation is always negative. The energy correlation is further reduced in post Hartree-Fock methods like f. ex. Møller Plesset pertubation theory, configuration interaction and coupled cluster.

2.2 Density Functional Theory (DFT)

2.2.1 Electron density

A different approach to finding the energy, of a system of particles, is to describe it as a density of electrons $\rho(\vec{r})$. Using the Born-Oppenheimer approximation the electron density can be explained as

$$\rho(\vec{r}_1) = N \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi(\vec{x}_1, \ldots, \vec{x}_N)|^2 d\sigma_1 d\vec{x}_2 \ldots d\vec{x}_N \tag{2.25}$$

This reduces the wave function down to 3 coordinates, x, y and z, from 4N coordinates. Integrating the density will give the total number of electrons in the system.

$$\int \rho(\vec{r}) d\vec{r} = N \tag{2.26}$$

2.2.2 The Hohenberg-Kohn Existence Theorem

The Hohenberg-Kohn existence theorem states that there is only one external potential $v(\vec{r})$ for a given ground state density $\rho(\vec{r})$. To prove the statement we assume two external potentials $v(\vec{r})$ and $v'(\vec{r})$ would give the same ground state density $\rho(\vec{r})$. This can be denoted in a short scheme

$$N, v(\vec{r}) \longrightarrow H \longrightarrow \psi \longrightarrow \rho(\vec{r}) \tag{2.27a}$$

$$N, v'(\vec{r}) \longrightarrow H' \longrightarrow \psi' \longrightarrow \rho(\vec{r}) \tag{2.27b}$$

where the difference between $\hat{H}$ and $\hat{H}'$ is the difference between the external potential.

$$\hat{H} = \hat{H}' - \sum_i (v'(\vec{r_i}) - v(\vec{r_i})) \tag{2.28}$$

By applying the variational theorem on the wave function in Equation 2.27a and substituting the Hamiltonian we get

$$\langle \Psi | \hat{H} | \Psi \rangle = E_0 < \langle \Psi' | \hat{H} | \Psi' \rangle =$$

$$\langle \Psi' | \hat{H}' | \Psi' \rangle - \sum_i^n \langle \Psi' | (v'(\vec{r_i}) - v(\vec{r_i})) | \Psi' \rangle = E_0' - \int_{-\infty}^{\infty} \rho(\vec{r})(v'(\vec{r_i}) - v(\vec{r_i}))d\vec{r} \tag{2.29}$$

By following the same procedure with Equation 2.27b and adding them up, we get

$$E_0 + E_0' < E_0' - \int_{-\infty}^{\infty} \rho(\vec{r})(v'(\vec{r_i}) - v(\vec{r_i}))d\vec{r} + E_0 - \int_{-\infty}^{\infty} \rho(\vec{r})(v(\vec{r_i}) - v'(\vec{r_i}))d\vec{r} \tag{2.30}$$

The energy contribution from the integrals cancel each other out and we are left with

$$E_0 + E_0' < E_0' + E_0 \tag{2.31}$$

which is a contradiction and we can find the energy of a molecule using the ground state density, as it holds all the information. The energy of the system can then be expressed as a functional of the ground state as

$$E[\rho(\vec{r})] = \int_{-\infty}^{\infty} \rho(\vec{r})v(\vec{r})d\vec{r} + T_e[\rho(\vec{r})] + V_{ee}[\rho(\vec{r})] \tag{2.32}$$

where the last two functional is combined to $E_{HK}[\rho(\vec{r})]$, which is unknown.

2.2.3 The Hohenberg-Kohn Variational Theorem

We introduce the variational principle to the density. This gives for a trial density $\rho'(\vec{r})$ an energy that is never less than the ground state energy.

$$E[\rho'(\vec{r})] \geq E[\rho(\vec{r})] = E_0 \tag{2.33}$$

By applying the constraint that the number of electrons is constant under changing of the density, we can minimize $E[\rho'(\vec{r})]$ by applying the lagrange multiplier.

$$\mathscr{L}[\rho'(\vec{r})] = E[\rho'(\vec{r})] - \mu \left(\int_{-\infty}^{\infty} \rho'(\vec{r})d\vec{r} - N \right) \tag{2.34}$$

We then change the trial density by an amount $\delta\rho'(\vec{r})$, which is non zero, and implementing Equation 2.32 we get

$$\frac{\delta E[\rho(\vec{r})]}{\delta\rho(\vec{r})} = \frac{\delta E_{HK}[\rho(\vec{r})]}{\delta\rho(\vec{r})} + v(\vec{r}) = \mu \tag{2.35}$$

where μ is the Lagrangian multiplier which describes the chemical potential of the system, for a neutral molecule it can be derived to be zero.

$$\mu = v(\vec{r}) + \frac{\partial E_{HK}[\rho]}{\partial\rho(\vec{r})} \tag{2.36}$$

2.2.4   Kohn-Sham equations

Since there is no direct way to make progress on Equation 2.36 and E_{HK} is large unknown value, we introduce a hypothetical reference system to reduce the unknown energy. This system is made of n non-interacting electrons in the external potential $v_{ref}(\vec{r})$. The potential is selected so that the reference density is identical to the true density of the system and the Hamiltonian can be expressed as

$$\hat{H}_{KS} = \sum_i^n h_i^{KS} = \sum_i^n \left(-\frac{1}{2}\nabla_i^2 + v_{ref}(\vec{r}) \right) \tag{2.37}$$

where KS stands for Kohn-Sham. We then introduce one electron Kohn-Sham spin orbitals ϕ_i^{KS} which are eigenfunction to the Kohn-Sham Hamiltonian

$$h^{KS}(1)\phi_i^{KS}(1) = \epsilon_i^{KS}(1)\phi_i^{KS}(1) \tag{2.38}$$

and the reference density can be expressed by these orbitals

$$\rho_{ref}(\vec{r}) = \sum_i^n |\phi_i(\vec{r})|^2 \tag{2.39}$$

We then add and subtract the Kohn-Sham Hamiltonian in Equation 2.32 the ground state energy can be expressed as

$$E[\rho(\vec{r})] = \int_{-\infty}^{\infty} \rho(\vec{r})v(\vec{r})d\vec{r} + T_{ref}[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})] \tag{2.40}$$

where E_{XC} is the remaining error expressed as

$$E_{XC} = T - T_{ref} + V_{ee} - J \tag{2.41}$$

and J is the Coulomb interactions which can be shown from the electron-electron repulsion with an added error.

$$E_{ee} = \frac{1}{2}\iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}d\vec{r}d\vec{r}' + \Delta E_{ee} = J[\rho(\vec{r})] + \Delta E_{ee} \tag{2.42}$$

Likewise for the HF technique we combine the functionals together as

$$f^{KS}(i) = h^{KS}(i) + J(i) + E_{XC}(i) \tag{2.43}$$

and introducing Atomic orbitals as a basis we obtain Roothaan-Hall equations like with HF

$$\mathbf{F^{HK}C} = \mathbf{SC}\epsilon \tag{2.44}$$

The system can be solved iterated and is as cheap as HF, however DFT includes correlation.

2.2.5 Exchange correlation

The correlation term can be expressed in a ladder of approximation. However, the approximation removes variational concept and DFT can therefore give energies bellow the true value. Also the order on the ladder does not mean it will always be better. Further the exchange correlation energy is often split in two different contributions.

$$E_{XC} = E_X + E_C \tag{2.45}$$

where the exchange is sometimes assumed to be grater than the correlation. The first of the approximation is called the local density approximation (LDA) and assumes an uniform electron gas and the exchange correlation can be expressed as

$$E_{XC} = \int f(\rho(\vec{r}))d\vec{r} \tag{2.46}$$

this approximation works well for metals and semi-conductors as they have a relative uniform electron density, however not as reliable for molecules with abrupt density changes. This can be compensated by introducing a gradient $\nabla\rho$, which is known as the general gradient approximation (GGA). Example of this is the Perdew-Becke-Ernzerhof and Becke exchange Lee-Yang-Parr correlation. Further we have the Meta - GGA, which includes the second derivative.

$$E_{XC} = \int \rho(\rho, \nabla\rho, \nabla^2\rho, \tau)d\vec{r} \tag{2.47}$$

where τ is the kinetic energy density, given as $\sum_i |\nabla\phi_i|^2$. And lastly we have the hybrid and double hybrid functional where the first include exact exchange from Hartree Fock partially, example B3LYP and PBEO. And the later include some correlation from post Hartree Fock techniques. However, this include the scaling of the system. The DFT can also be expanded to include other approximation like time dependance.

2.3 Density Functional Based Tight Binding (DFTB)

2.3.1 Tight Binding (TB)

HF and DFT are ab initio method, meaning 'from the beginning', and there accuracy depends on the method used. However, some exchange-correlation functionals in DFT use empirical parameters and therefore not always considered as an ab initio method. For larger systems ab initio methods can be quite demanding and semi-empirical methods are developed where they simplify the Hamiltonian and adjust parameters based on experimental data. DFTB is an semi-emperical methode parametrized on DFT, using linear combination atomic orbitals (LCAO). The total energy in a tight binding scheme is

$$E = E_{bnd} + E_{rep} \tag{2.48}$$

where E_{bnd} is the sum of all occupied orbital energy derived from diagonalization of the electronic Hamiltonian and E_{rep} is a repulsive contribution of atomic pairs. TB uses atomic orbitals which can be expressed like Equation 2.21 in a small basis which reduces the time of calculation. For an non-orthonormal basis we get secular equations to solve

$$\sum_{ab} c_a i \left(H_{ab} - \epsilon_i S_{ab}\right) \tag{2.49}$$

2.3.2   From DFT to DFTB

DFTB expands around a reference density $\rho_0(\vec{r})$ using a Taylor expansion, and the total density can be written as $\rho(\vec{r}) = \rho_0(\vec{r}) + \delta\rho(\vec{r})$. By adopting the energy found in KS-equations (Equation 2.40), energy up to the third order can be expressed as

$$
E^{DFTB3}[\rho_0 + \delta\rho] = V_{NN} - J[\rho] - \int v(\vec{r})p_o(\vec{r})d\vec{r} + E_{XC}[p_0]
$$

$$
+ \sum_i n_i \langle \psi_i | \hat{H}[p_0] | \psi_i \rangle + \frac{1}{2} \iint \left(\frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{XC}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')}\bigg|_{\rho_0} \right) \delta\rho(\vec{r})\delta\rho(\vec{r}')d\vec{r}d\vec{r}'
$$

$$
+ \frac{1}{6} \iiint \frac{\delta^3 E_{XC}[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')\delta\rho(\vec{r}'')}\bigg|_{\rho_0} \delta\rho(\vec{r})\delta\rho(\vec{r}')\delta\rho(\vec{r}'')d\vec{r}d\vec{r}'d\vec{r}''
$$

$$
= E^0[\rho_0] + E^1[\rho_0, \delta\rho] + E^2[\rho_0, (\delta\rho)^2] + E^3[\rho_0, (\delta\rho)^3]
$$

(2.50)

where the first line is double counting contribution and V_{NN} which is approximated as the repulsive energy from pair interaction $E_{rep} = \frac{1}{2} \sum_{ij} V_{ij}$. The later terms are build hierarchy where each addition will lead to different DFTB methods. The first of this is DFTB1 or DFTB contains only the first energy, the band energy, which consist of the Kohn-Sham Hamiltonian over the reference density. The energy is using TB expressed as

$$
E^1[\rho_0, \delta\rho] = \sum_i \sum_{ab} n_i c_{ai} c_{bi} H_{ab} = \sum_g n_i \epsilon_i
$$

(2.51)

For DFTB1 this gives energies as with a approximated repulsive contribution fitted to empirical data or compared with DFT calculations. The main advantage with this approach is that Kohn-sham equations are solved only ones. Furthermore, the method is non-self-consistent, unlike DFTB2-3, making it a fast method and is suitable for system with small charge transfers or a complete charge transfer. DFTB2 or self-consistent charge DFTB and DFTB3 uses the density fluctuation as a superposition of atomic contribution

$$
\delta\rho = \sum_a \delta\rho_a
$$

(2.52)

Each of these atomic orbital fluctuations is expanded further in a multipole expansion, but approximated using only the monopole term

$$
\delta\rho_a \approx \Delta q_a F_{00}^a Y_{00} \approx \Delta q_a \frac{\tau_a^3}{8\pi} e^{-\tau_a|\vec{r} - \vec{R}_a|}
$$

(2.53)

where δq denotes atomic charge fluctuation, F_{00} denotes the radial dependence with a corresponding angular function Y_{00}. This can be further approximated to the last term by assuming exponential decay, where $\tau_a = \frac{16}{5} U_a$ in which U_a is the Hubbard parameter related to the chemical hardness of the atom. E^2 and E^3 can be written as

$$
E^2 = \frac{1}{2} \sum_{ab} \gamma_{ab} \Delta q_a \Delta q_b
$$

(2.54a)

$$
E^3 = \frac{1}{6} \sum_{abc} \Delta q_a \Delta q_b \Delta q_c \frac{\delta\gamma_{ab}}{\delta q_c} = \frac{1}{3} \sum_{ab} \Delta q_a^2 \Delta q_b \Gamma_{ab}
$$

(2.54b)

where $\Gamma = \delta\gamma_{ab}/\delta q_b|_{q_a^0}$ and γ is

$$\gamma_{ab} = \iint \frac{1}{|\vec{r} - \vec{r'}|} \frac{\tau_a^3}{8\pi} e^{-\tau_a |\vec{r} - \vec{R}_a|} \frac{\tau_b^3}{8\pi} e^{-\tau_b |\vec{r'} - \vec{R}_b|} \qquad (2.55)$$

The Hamiltonian for the DFTB2-3 scheme can be expressed as

$$H_{ab}^{DFTB2-3} = H_{ab}^0 + S_{ab} \sum_c \Delta q_c \left(\frac{1}{2}(\gamma_{ac} + \gamma_{bc}) + \frac{1}{3}(\Delta q_a \Gamma_{ac} + \Delta q_b \Gamma_{bc}) + \frac{\Delta q_c}{6}(\Gamma_{ca} + \Gamma_{cb}) \right) \quad (2.56)$$

which for DFTB2 only contains the first term in the Secular term. The Hamiltonian found need then to be solved using Equation 2.49. The correction energy in DFTB2 allows treatments of charge transfer effects and DFTB3 correction gives an additional flexibility, like proton affinities. Further the scheme can be expanded to include some of its weakness like dispersion. These are non-covalent interactions, Spin-polarized, self-interaction correction scheme, long range corrected DFTB, time dependent DFTB, hybrid and QM-MM methods.

3   Discussion

3.1   Approximations in DFT and HF

The Born-Oppenheimer approximation is a core approximation for computational chemistry, and in general holds well for calculating energies for fixed nucleus. However, there are two major application in which it breaks down. This is for non-adiabatic chemical behaviour, ex. metal surfaces and electron transfer, and exotic molecules where the electron is exchanged with heavier particles. In general the approximation does not lead to a great defecate, but techniques can be expressed to demonstrate edge cases. This applies for the time variable which will not be discussed.

Other major approximations are the uses of finite basis sets and the mean field approximation. Depending on the basis set used there will be an error to the energy. Therefore, there is a lot of work on different basis sets. These sets can be categorised in groups with a hierarchy, where more orbitals is better. Choice of these basis sets depends on the wanted accuracy and time available. The mean field approximation is what gives us the exchange correlation error. When comparing the HF and DFT, DFT include the correlation energy given the same computational cost. However, by doing so DFT loses its variational property and some of these approximations increase the computational cost by including post HF methods. HF can compensate this by including post-HF methods. However, the scaling of the computation increases as the accuracy is increased.

3.1.1   DFTB as a technique

DFTB is parameterise from DFT meaning it will adopt all of its properties. It also makes some new approximations from tight binding. These approximation will make DFTB less accurate then DFT and post-HF methods. The first DFTB method is Good at describing systems where there is no/small or complete charge transfers, while DFTB2-3 can handle these systems. Since DFTB1 is non-self-consistent it is only solved once, where as DFTB2-3 need multiple iterations. However, the reduction in computational time is what makes the DFTB schemes strong. And likewise for DFTB it can be expanded to improve accuracy on its weaknesses.

3.1.2   Application and accuracy of DFTB

The application of the DFTB are many, one of the application is on small molecules, which is used as building blocks for larger systems. This is a mean of bench marking different DFTB schemes to check its accuracy vs DFT and HF techniques. Since the application can

be addressed on a lot of different systems of particle, there is no good way to summarise. Depending on the system you can get a large or small deviation of the system, where for some it is in the threshold for chemical accuracy. However, DFTB is designed for larger systems.

As large systems is one of main driver behind the development of DFTB, system larger then that of DFT, while maintaining an electronic scale description. These range from large molecules, biomolecules, different clusters, nanoparticles and supported/embedded systems. DFTB shows good results in its applications of cluster, where it noted that Au_{55} hold cavities, which has been confirmed by two DFT studies. It also prevails at water cluster which is of significant interest of understanding solvation.

DFTB is also used for vibrational spectroscopy, reactivity, fragmentation, thermodynamics and exited states. The use of vibrational spectroscopy is an important issue as it allows for better diagnostic for presence of species in samples. For thermodynamics it has been of interest to study the evolution of structural properties under the change of temperature, as well as heat capacities.

The results of the different application are too many to condense in one paper. Therefore, it will be useful to dive in specific category of interest to see how it compares to the designated use. DFTB techniques are under continuous development as not all elements are parameterised, expansion of new orders. DFTB has not been compared to other semi-empirical methods, which can be better. Therefore, for a given system DFTB should be a consideration.

4   Conclusion

DFTB is a method that parameterize the DFT through a taylor expansion of a referance density. From this there have been developed techniques up to the third order, as well as methods to improve the shortcomings that DFTB holds. The accuracy depends on the systems, but most are covered and is very accurate on some fields, and therefore should always be considered when computing systems. [2;3;4;5;6;7;8;9;9;10;11;12;13;14;15;16;17;18;19;20;21;22;23;1;24;25;26;27;1;28;29;30;31]

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