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Hartree-Fock and Density Functional Theory methods for Molecular Geometry Optimization

Bachelor's thesis in Chemistry
Supervisor: Marcus Takvam Lexander

April 2023

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Abstract

In this thesis, Hartree-Fock and density functional theory are examined for use in geometry optimization procedures. The theory behind Hartree-Fock and DFT is thoroughly described, and a molecular gradient expression is derived for Hartree-Fock. A benchmarking study by Brémond and coworkers[1] is used as a basis for discussion of 62 exchange-correlation functionals, including HF and three post-HF methods, where only MP2 is discussed. The ECFs are discussed using the results from this and other studies, and their respective common challenges.

Contents

Introduction

In electronic structure theory, one aims to solve the time-independent Schrödinger equation (1.1) to find the electronic wavefunction and energy of the system in question[2]. This has various applications, two of them being geometry optimization[3;4] and response theory[5]. Because of the complexity of the equation, methods of varying accuracy and sophistication, levels of theory, are used to calculate this energy[6]. Before the days of quantum chemistry, spectroscopic methods were used to find energies and structures of molecules and atoms. A theoretical method for determining geometries at a lower level of theory, is the valence shell electron pair repulsion (VSEPR) theory, which uses the electrostatic repulsion of localized electron pairs to explain 3D structures of molecules and complexes[7]. While spectroscopic methods have improved since its early days in the 1800s[8], the development of ab initio quantum mechanical calculations have improved our understanding, not only of atomic and molecular structure, but also of the processes behind the spectroscopic methods used to obtain the same results[9].

Geometry optimization is of great importance in quantum chemistry because it predicts the geometry a molecule is most likely to have at a given time. This can help explain molecular properties and reactions. The equilibrium geometry is found when the energy is at a minimum. Multiple methods can be used for this, but the gradient method proposed by Pulay[10] is an effective and widely used method. Geometry optimization has many applications, including calculating spectroscopic data[11]. This can be used for predicting the stability of structures an derivatives[12] or chromophores[13]. Other applications include optical rotation[14], calculating bond lengths of polymers[15] and calculations of organic crystal structures[16].

There are two views on electronic structure theory, wave function theory (WFT) and density functional theory (DFT), where DFT can be seen as an approximation of WFT. The wavefunction theories include Hartree-Fock and post Hartree-Fock methods of approximation[2]. These use the wavefunctions of electrons to find properties of the system, while DFT uses the electron probability densities. Importantly, WFT generally yields quite complicated equations, and can thus only be used for relatively small systems without being too time-consuming and expensive. Even then, the Schrödinger equation is impossible to solve exactly, and approximations have to be done.

According to the Hohenberg-Kohn existence theorem, it is possible to find the exact solution to the Schrödinger equation, using density functional procedures[17]. Unfortunately, DFT is dependent on an exchange-correlation term that is still unknown today, sixty years after the theorem was first proposed. Because of this, many approximate exchange-correlation functionals (ECFs) have been proposed, but no one has found one that performs uniformly well for all systems and all applications. This causes a split in the DFT-community, where some say that finding empirical functionals that work well for a specific result for a specific

system is sufficient, and others are looking for the universal functional that will bring us closer to the exact solution of the Schrödinger equation. According to Medvedev and coworkers, the empirical fitting of ECFs is obstructing the path towards the exact functional[18].

This thesis will go through both Hartree-Fock theory, density functional theory and the expression for the Hartree-Fock molecular gradient. General challenges for Hartree-Fock and DFT are presented and discussed. A study by Brémond et al.[1] is used as a basis for discussion of different exchange-correlation functionals, including Hartree-Fock and MP2. The mathematical background of the functionals will not be thoroughly discussed beyond the Hartree-Fock equations and the exact part of DFT.

1 Fundamental quantum chemistry

The overall goal in electronic structure theory is to solve the time-independent Schrödinger equation,

$$\hat{H}\Psi(\mathbf{x}) = E\Psi(\mathbf{x}) \tag{1.1}$$

where $\hat{H}$ is the Hamiltonian, $\Psi(\mathbf{x})$ is the wavefunction and E is the energy of the wavefunction[2]. This is a pretty simple task for a system of only one electron. However chemists are usually interested in larger systems, like molecules, proteins, polymers etc. For these systems, the Schrödinger equation cannot be solved exactly. Because of this, there is a need for approximations and computational methods.

The molecular Hamiltonian is an operator that works on the system to return its energy[2]. It contains the kinetic energy of the nuclei and electrons, the repulsion between two nuclei, the repulsion between two electrons, and the attraction between electrons and nuclei. Mathematically it is defined as the sum of these operators (eq. 1.2).

$$\hat{H} = \hat{T_N} + \hat{T_e} + \hat{V}_{NN} + \hat{V}_{ee} + \hat{V}_{eN} \tag{1.2}$$

The first simplification to the Schrödinger equation is the Born-Oppenheimer approximation[2]. It states that since the nuclei are much heavier than the electrons, the nuclei move very slowly relative to the electrons, and can be treated as stationary. The Hamiltonian is then separated into a nuclear and an electronic part. The resulting equation is the electronic Schrödinger equation,

$$\hat{H}_e\Psi_e(\mathbf{r};\mathbf{R}) = E_e(\mathbf{R})\Psi_e(\mathbf{r};\mathbf{R}) \tag{1.3}$$

where the Hamiltonian is

$$\hat{H}_e = -\frac{1}{2}\sum_i^N \nabla_i^2 - \sum_i^N\sum_I^{N_n} \frac{Z_I}{r_{Ii}} + \frac{1}{2}\sum_{i\neq j}^N \frac{1}{r_{ij}} + \frac{1}{2}\sum_{I\neq J} \frac{Z_IZ_J}{r_{IJ}} \tag{1.4}$$

in atomic units[6]. The first term is the kinetic energy of the electrons, where ∇^2 is the Lagrangian, the second derivative with respect to all spacial coordinates. The second term is the attraction between electrons and nuclei, where r_{Ii} is the distance between electron i and nucleus I, and Z_I is the charge of nucleus I. The third term is the repulsion between electron i and j, where r_{ij} is the distance between electrons. The last term is the nucleus-nucleus repulsion. N and N_n are the number of electrons and nuclei, respectively. The repulsion between nuclei often regarded as constant in the Born-Oppenheimer approximation, and is usually added in the end.

The Born-Oppenheimer approximation yields a potential energy for the electron as a function of the nuclei coordinates. This is the potential energy surface (PES)[19]. It contains information about possible chemical reactions, molecular vibrations and the dissociation energy[6]. For this thesis, the most important information contained in the potential energy surface is the equilibrium geometry. That is the geometry where the energy of the system is at a minimum. An expression for this will be derived for Hartree-Fock theory.

1.1   Orbital notation

For single atoms, two electrons occupy the same atomic orbital (AO), χ_μ[2]. These are extended to molecular orbitals (MOs), ψ_p, through the linear combinations of atomic orbitals (LCAO) expansion, shown in equation 1.5.

$$\psi_p(\mathbf{r}) = \sum_{\mu=1}^{N} C_{\mu p} \chi_\mu(\mathbf{r}) \tag{1.5}$$

$C_{\mu p}$ is a constant which decides the weighting of the AOs. MOs are further extended to spin orbitals (SOs), ϕ_i, by multiplication with the spin function, $\sigma(\omega)$, according to equation 1.6[6].

$$\phi_i(\mathbf{x}) = \psi_p(\mathbf{r}) \cdot \omega(\sigma) \tag{1.6}$$

The spin function is defined as

$$\omega(\sigma) = \begin{cases} \alpha(\sigma) \\ \beta(\sigma) \end{cases}$$

where α and β are required orthonormal.

2 Hartree-Fock

In this section the principles of Hartree-Fock (HF) theory will be presented. This thesis will be limited to the discussion of restricted Hartree-Fock (RHF), where only closed-shell states are considered[6], but unrestricted Hartree-Fock for open-shell systems could also be discussed.

2.1 The Variational principle

The variational principle is a useful way of optimizing the wavefunction[6]. The energy of a trial wavefunction, ψ_{trial}, is calculated using the Hamiltonian. This will energy will always be higher than or equal to the true ground-state energy of the system, E_0, as shown in equation 2.1.

$$\frac{\langle \psi_{trial} | H | \psi_{trial} \rangle}{\langle \psi_{trial} | \psi_{trial} \rangle} \geq E_0 \tag{2.1}$$

The left side of this inequality, sometimes called the Rayleigh ratio, is then differentiated and minimized with respect to MO coefficients to get the lowest possible energy. This yields the optimum wavefunction, and an upper bound to the energy of the wavefunction.

2.2 Self-consistent fields and the Hartree-Fock equations

The basis of Hartree's wavefunctional theory[20] for N-electron systems is that the electron to be calculated experiences a combined, average potential from the other N-1 electrons and the nuclei. This is called mean fields[21]. For an N-electron system, the Hamiltonian, $\hat{H}$, is separated into N one-electron Hamiltonians, $\hat{h}_i$, as shown in equation 2.2.

$$H(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = h_1(\mathbf{x}_1) + h_2(\mathbf{x}_2) + ... + h_N(\mathbf{x}_N) \tag{2.2}$$

In order to ensure antisymmetry and obey the Pauli principle, the HF wavefunction is approximated by a Slater determinant of the spin orbitals[22]. A matrix consisting of spinorbitals, $\phi_i(\mathbf{x})$, is constructed, where the columns are distinct spin-parts and the rows are spin orbitals. The determinant is calculated as in equation 2.3[6].

$$\Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_a(1) & \phi_b(1) & \dots & \phi_z(1) \\ \phi_a(2) & \phi_b(2) & \dots & \phi_z(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_a(N) & \phi_b(N) & \dots & \phi_z(N) \end{vmatrix} \tag{2.3}$$

The determinant which is found is called the Hartree-Fock determinant, Φ_{HF}. This is the wavefunction which is minimized using the variational principle.

The Fock operator, $\hat{f}$, is made up of a one-electron part and a two-electron part (eq. 2.4),

$$\hat{f}_1 = h_1 + \sum_j \{2J_j(1) - K_j(1)\} \tag{2.4}$$

where $\hat{J}_j(1)$ is the Coulomb operator, and accounts for the repulsion between electrons[21]. The exchange operator, $\hat{K}_j(1)$ accounts for the exchange interaction between equal spin states, specifically stabilizing the system when two electrons have unpaired spins, and was introduced by Fock[23]. They are defined in equations 2.5 and 2.6[6].

$$J_j(1)\psi_i(1) = \int \psi_j^*(2)\frac{1}{r_{12}}\psi_i(1)\psi_j(2)d\tau_2 \tag{2.5}$$

$$K_j(1)\psi_i(1) = \int \psi_j^*(2)\frac{1}{r_{12}}\psi_j(1)\psi_i(2)d\tau_2 \tag{2.6}$$

The Fock operator acts on the wavefunction to form a pseudo-eigenvalue equation, which yields the diagonal matrix of orbital energies, ε_i, as the pseudo-eigenvalue.

$$f_1\psi_i(1) = \varepsilon_i\psi_i(1) \tag{2.7}$$

Equation 2.7 are the canonical Hartree-Fock equations, where $\psi_i(1)$ are the orbital wavefunctions. These can be solved numerically for AOs, but for MOs, the Roothaan-Hall equations are used, as shown in equation 2.8 in AO basis.

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{2.8}$$

$\mathbf{F}$ is the Fock matrix, and $\mathbf{S}$ is the overlap matrix of atomic orbitals. Their elements are shown in equations 2.9 and 2.10, respectively.

$$F_{\mu\nu} = \langle \chi_\mu(1)|f_1|\chi_\nu(1)\rangle \tag{2.9}$$

$$S_{\mu\nu} = \langle \chi_\mu(1)|\chi_\nu(1)\rangle \tag{2.10}$$

$\mathbf{C}$ is the matrix of MO coefficients from equation 1.5.

The Roothaan-Hall equations are solved using the self consistent field (SCF) method[6]. This is an iterative process, where the wavefunction is improved by each iteration[21]. Solving the Roothaan-Hall equations requires an initial guess of the wavefunction within a chosen basis. The Hartree-Fock SCF calculation is done as shown in figure 2.1.

Typically, convergence is said to be reached when $\mathbf{C}' = \mathbf{C}$. In reality however, the MO coefficients might not converge even though the Fock matrix yields sufficient energies. Because of this, convergence acceleration is done to reduce the number of iterations, typically DIIS[24;25;26].

From the Slater-Condon rules[6], the Restricted Hartree-Fock energy expression becomes,

$$E_{RHF} = 2\sum_i h_{ii} + \sum_{i \neq j}(2g_{iijj} + g_{ijji}) + h_{nuc} \tag{2.11}$$
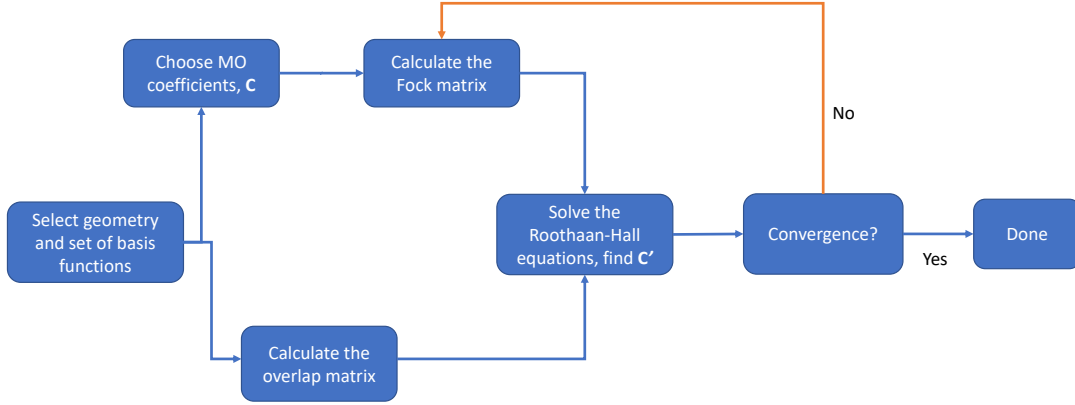
Figure 2.1: A flow chart depicting the iterations of the Hartree-Fock self-consistent field calculation.

where g_{iijj} is the coulomb contribution and g_{ijji} is the exchange contribution to the energy in MO basis. h_i is the one-electron contribution and h_{nuc} is the contribution from the nuclei. This energy is invariant to orbital rotation among the occupied orbitals, meaning that alternative sets of orbitals can be used to minimize the energy, if they maintain their orthogonality[27]. This can for example be used for localizing orbitals. The HF energy can be rewritten in terms of the AO density matrix (eq. 2.12)[10].

$$E_{RHF} = 2\text{Tr}[\mathbf{Dh}] + \text{Tr}[\mathbf{DG(D)}] + h_{nuc} \tag{2.12}$$

where $\text{Tr}[\mathbf{A}]$ is the sum of the diagonal elements, trace, of a general matrix $\mathbf{A}$[28]. The density matrix $\mathbf{D}$ is defined as

$$\mathbf{D} = \mathbf{C}_o \mathbf{C}_o^T \tag{2.13}$$

where $\mathbf{C_o^T}$ is the transpose of $\mathbf{C_o}$, which is the coefficient matrix for occupied orbitals. $\mathbf{G(D)}$ is the two-electron part of the energy expression,

$$G_{\mu\nu}(D) = \sum_{\rho\sigma}(2g_{\mu\nu\rho\sigma} - g_{\mu\nu\sigma\rho})D_{\rho\sigma} \tag{2.14}$$

3   Density Functional Theory

In density functional theory (DFT), the Hamiltonian is defined as in equation 3.1[17].

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}v(\mathbf{r}_i) + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \hat{T} + \hat{V}_{ext} + \hat{V}_{ee} \tag{3.1}$$

This is similar to the Hamiltonian in the Born-Oppenheimer approximation (eq. 1.4), as $\hat{T}$ is the kinetic energy part, $\hat{V}_{ext}$ is the potential between the nuclei and the electrons, and $\hat{V}_{ee}$ is the electron-electron repulsion[6].

DFT uses electron density in place of wavefunctions, which is defined as the electron probability density of N electrons,

$$\rho(\mathbf{r}) = N \int \cdots \int |\Psi(\mathbf{r_1}\sigma_1, ..., \mathbf{r}_N\sigma_N)|^2 d\mathbf{r}_2...d\mathbf{r}_N d\sigma_1...d\sigma_N, \qquad (3.2)$$

where N is a normalization constant[17].

3.1 The Hohenberg-Kohn theorems

The Hohenberg-Kohn existence theorem states that

> The ground-state energy and all other ground-state electronic properties are uniquely determined by the electron density[6].

The DFT energy expression is

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \qquad (3.3)$$

where $v(\mathbf{r})$ is defined mathematically as in equation 3.4, which is analogous to the second term in equation 1.4.

$$v(\mathbf{r}) = -\sum_I^{N_n} \frac{Z_I}{|\mathbf{r} - \mathbf{r}_I|} \qquad (3.4)$$

V_{ee} can be separated into a classical and a non-classical term, according to the equation,

$$E_{ncl}[\rho] = V_{ee}[\rho] - J[\rho] \qquad (3.5)$$

where the classical functional $J[\rho]$, is defined similarly to the Coulomb interaction in HF (eq. 2.5), and is the major contribution. It is given in equation 3.6.

$$J[\rho] = \frac{1}{2} \iint \rho(1)\frac{1}{|\mathbf{r} - \mathbf{r}'|}\rho(2)d\mathbf{r}d\mathbf{r}' \qquad (3.6)$$

The Hohenberg-Kohn variational theorem, like the variational theorem for wavefunctions, states that

> For a trial density function $\rho'(\mathbf{r})$, the energy functional $E_0[\rho']$ cannot be less than the true ground-state energy of the molecule[6].

This means that there exists an upper bound for the ground state energy for a specific electron density, and the variational principle can be used to find the optimum electron density.

3.2   The Kohn-Sham equations

In Kohn-Sham theory, a chosen external potential, $v_{ref}(\mathbf{r})$, yields a reference electron density, $\rho_{ref}(\mathbf{r})$ that is equal to the true electron density of the N-electron system, $\rho(\mathbf{r})$[6]. This is done in orbital representation, where the Kohn-Sham orbitals form a Slater determinant (equation 2.3) made from the N occupied orbitals[17]. The Hamiltonian of the reference state is given as a sum over the N one-electron Kohn-Sham Hamiltonians, given in equations 3.7 and 3.8.

$$h_{ref} = \sum_{i=1}^{N} h_i^{KS} \tag{3.7}$$

$$h_i^{KS} = -\frac{1}{2}\nabla_i^2 + v_{ref}(\mathbf{r}_i) \tag{3.8}$$

Acting the Kohn-Sham Hamiltonian on Kohn-Sham orbitals, ψ_m^{KS}, gives an eigenvalue equation called the Kohn-Sham equation, where the orbital energy is the eigenvalue (eq. 3.9).

$$h_i^{KS}\psi_m^{KS}(i) = \varepsilon_m^{KS}\psi_m^{KS}(i) \tag{3.9}$$

This is only for the reference system. The energy functional of the reference system is given in equation 3.10.

$$E_{ref}[\rho_{ref}] = T_{ref}[\rho_{ref}] + V_{ee,ref}[\rho_{ref}] + \int \rho_{ref}(\mathbf{r})v_{ref}(\mathbf{r})dr \tag{3.10}$$

This is extended to real systems by separating $V_{ee}[\rho]$ into a Coulomb and an exchange-correlation part. Since the reference electron density and the real electron density are the same, and the reference potential is chosen to be the real external potential, equation 3.10 can be further simplified into equation 3.11[6].

$$E[\rho] = T_{ref}[\rho] + J[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})dr + E_{XC}[\rho] \tag{3.11}$$

where the exchange correlation functional is defined as in eq. 3.12.

$$E_{XC}[\rho] = T[\rho] + V_{ee}[\rho] - (T_{ref}[\rho] + J[\rho]) \tag{3.12}$$

The effective potential is defined as

$$v_{eff} = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + v_{XC}(\mathbf{r}) \tag{3.13}$$

where $v_{XC}(\mathbf{r})$ is the exchange-correlation part of the potential, which must be equal to the reference potential to solve the Kohn-Sham equation. Rewriting the Hamiltonian, by substituting equation 3.13 into the equation for the KS Hamiltonian, eq. 3.8, the Kohn-Sham Hamiltonian is redefined to equation 3.14.

$$h_i^{KS} = h_1 + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + v_{XC}(\mathbf{r}) \tag{3.14}$$

where h_1 is the same one-electron Hamiltonian as in HF. h_i^{KS} is analogous to the Fock operator[29]. Inserting this into equation 3.9, yields

$$\mathbf{h}_{KS}\mathbf{C} = \mathbf{S}\mathbf{C}\varepsilon \tag{3.15}$$

in the AO basis, where the $\mathbf{h}_{KS}$ works like the Fock matrix in HF,

$$h_{\mu\nu} = \langle \chi_\mu(1)|\mathbf{h}_{KS}|\chi_\nu(1)\rangle \tag{3.16}$$

and $\mathbf{S}$ is the atomic overlap matrix, defined in equation 2.10. The atomic orbitals are defined by the LCAO expansion for the Kohn-Sham orbitals. This equation is then solved iteratively, like the Roothaan-Hall equation in Hartree-Fock.

The Kohn-Sham energy contributions are given in 3.17.

$$E = E_T + E_V + E_J + E_{XC} \tag{3.17}$$

where E_T is the energy that arises from the kinetic energy operator, E_V is from nucleus-electron repulsion, E_J is the Coulomb repulsion and E_{XC} is the exchange-correlation energy. In terms of operators, the energy expression becomes

$$E_{KS} = \sum_i^N h_{ii} + \sum_{i\neq j} g_{iijj} + E_{XC} \tag{3.18}$$

This is very similar to the Hartree-Fock energy (equation 2.11). In fact, Hartree-Fock theory can be seen as a special case of DFT, where the exchange-correlation functional is given as the exchange term, K, and the correlation is zero. In matrix notation for the AO basis, the energy expression becomes

$$E_{KS} = 2\text{Tr}[\mathbf{D}\mathbf{h}] + \text{Tr}[\mathbf{D}\mathbf{J}] + E_{XC} \tag{3.19}$$

where $\mathbf{J}$ is the Coulomb matrix (eq. 3.20)[30] and $\mathbf{D}$ is the AO density matrix, given for HF in equation 2.13.

$$J_{\mu\nu} = \sum_{\lambda\sigma} D_{\lambda\sigma} \langle \mu\nu|\lambda\sigma\rangle \tag{3.20}$$

3.2.1   Exchange-Correlation functionals

The problem with DFT is calculating the exchange-correlation energy, $E_{XC}[\rho]$. This must be done to get the exchange-correlation potential, v_{XC}, which is included in the Kohn-Sham Hamiltonian. To obtain a result from DFT, the exchange-correlation energy thus has to be approximated, using an exchange-correlation functional, ECF. This is where most of the error in DFT stem from[17].

The simplest ECFs are the local density approximation functionals (LDA). The exchange-correlation energy is defined in LDA as

$$E_{XC}^{LDA}[\rho] = A \int \rho(\mathbf{r})^{4/3} d\mathbf{r} \tag{3.21}$$

where $A = -\frac{9}{8}\alpha(\frac{3}{\pi})^{1/3}$ and α is a tunable parameter, usually determined from fitting of experimental data. The exchange-correlation potential is then given in eq. 3.22.

$$v_{XC}(\mathbf{r}) = \frac{4}{3}A\rho(\mathbf{r}) \tag{3.22}$$

LDA is most accurate for metals and other systems where the uniform electron gas approximation describes the system best[17]. The generalized gradient approximation (GGA) is better suited to describe other systems with varying electron densities. E_{XC}^{GGA} is defined as

$$E_{XC}^{GGA}[\rho] = \int f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}))d\mathbf{r} \tag{3.23}$$

where ∇ is the gradient and f is a chosen function[6].

Extending the GGA functional to include the second derivative of the electron density, and occasionally the kinetic energy density $\tau(\mathbf{r})$, the meta-generalized gradient approximation (mGGA) is obtained (equation 3.24).

$$E_{XC}^{mGGA}[\rho] = \int f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \tau(\mathbf{r}))d\mathbf{r} \tag{3.24}$$

$\tau(\mathbf{r})$ is defined according to

$$\tau(\mathbf{r}) = -\frac{1}{2}\sum_i \int \psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r})d\mathbf{r} \tag{3.25}$$

For both GGA and mGGA the function f is often chosen according to experimental data.

The hybrid class of functionals uses the exchange energy from Hartree-Fock theory in the exchange part of E_{XC}. This can be used in combination with LDA, GGA or mGGA functionals. The resulting exchange-correlation functional is a linear combination of HF exchange energy in addition to other ECFs,

$$E_{XC}^{hybrid} = a_0 E_x^{HF} + (1 - a_0)E_x^{ECF} + E_c^{ECF} \tag{3.26}$$

where a_0 is a constant. This comes from the separability of E_{XC} to $E_X + E_C$.

Some specific functionals are shown in table 3.1.

Table 3.1: A selection of different exchange-correlation functionals used in chemistry, according to which family of functionals they belong in [17].

Class of functionals	Specific functionals
LDA	SVWN
	SVWN5
	SPL
GGA	BLYP
	BPW91
	PBE
mGGA	TPSS
	M06-L
Global hybrid	M06
	M06-2X
	B3LYP
Range separated hybrid	ωB97
	M11
	CAM-B3LYP
Double hybrid	xDH-PBE0
	B2π-PLYP
	PBE0-2

4 Geometry optimization

The goal of geometry optimization procedures is to find the optimum geometry of the molecule, which is found at the minimum of the potential energy surface [31]. The analytical way of finding a minimum is by differentiating with respect to each spacial coordinate. For a system of N coordinates, the differentiation thus needs to be over 3N Cartesian coordinates or 3N-6 internal coordinates [32]. Due to the complexity of large molecules, numerical methods are used. Some methods used are gradient descent, Newtons method and BFGS [33;34]. These are all gradient methods, with various rates of convergence. Newtons method is generally more accurate, but since it includes the Hessian, it is much more expensive than BFGS. Thus, BFGS is most used in practice.

Gradient descent uses the gradient of a function, ∇, to take steps of smaller and smaller size towards the minimum of the function.

$$f(x_{i+1}) = f(x_i) - \lambda \nabla f(x_i) \tag{4.1}$$

As the geometry converges, $\nabla f(x_i)$ gets smaller, and the optimum geometry is found. λ is a constant that determines the weighting of the gradient, and the size of the step. The optimum value of λ would be one over the second derivative of the function, which will yield Newtons method.

Finding the molecular gradient is an important first step in most geometry optimization procedures[10]. This will be done for HF in the next section, and it will be commented on for DFT.

4.1   Finding the gradient of the Hartree-Fock energy

For a Hartree-Fock calculation, all the nuclear coordinates $R = (X_1, X_2, ..., X_N)$ have to be evaluated for each atom. The Hartree-Fock energy is given in matrix form in equation 2.12. Because of the coefficient matrices, $C_{\mu p}$, this equation is costly to differentiate. The goal is to differentiate this expression, and to simplify equation 4.2.

$$E^{(1)} = \text{Tr}[2(\mathbf{Dh})^{(1)}] + \text{Tr}[(\mathbf{DG(D)})^{(1)}] + h_{nuc}^{(1)} \tag{4.2}$$

By using the product rule, the definition of the Fock matrix, $\mathbf{F} = \mathbf{h} + \mathbf{G(D)}$, and the chain rule on $\mathbf{DG(D)^{(1)}}$, equation 4.2 simplifies to

$$E^{(1)} = \text{Tr}[2\mathbf{Dh}^{(1)} + 2\mathbf{D}^{(1)}\mathbf{F} + \mathbf{DG}^{(1)}(\mathbf{D})] + h_{nuc}^{(1)} \tag{4.3}$$

Substituting $\mathbf{D}$ with $\mathbf{C}_o\mathbf{C}_o^T$, where $\mathbf{C}_o$ is the coefficient matrix for occupied orbitals, and combining eq. 4.3 with eq. 2.8, the second term in eq. 4.3 can be replaced as in eq. 4.4.

$$\text{Tr}[\mathbf{D}^{(1)}\mathbf{F}] = \text{Tr}[\varepsilon_0(\mathbf{C}_o^{(1)}\mathbf{SC}_o^T + \mathbf{C}_o^{(1)^T}\mathbf{SC}_o] \tag{4.4}$$

Using the orthonormality of the molecular orbitals, $\mathbf{C}_o^T\mathbf{SC}_o$ simplifies to the identity matrix, $\mathbf{I}^{[10]}$. Since the identity matrix is constant, the derivative is zero. The result of this is

$$(\mathbf{C}_o^T\mathbf{SC}_o)^{(1)} = \mathbf{C}_o^{(1)T}\mathbf{SC}_o + \mathbf{C}_o^T\mathbf{S}^{(1)}\mathbf{C}_o + \mathbf{C}_o^T\mathbf{SC}_o^{(1)} = 0 \tag{4.5}$$

which means

$$\mathbf{C}_o^{(1)T}\mathbf{SC}_o + \mathbf{C}_o^T\mathbf{SC}_o^{(1)} = -\mathbf{C}_o^T\mathbf{S}^{(1)}\mathbf{C}_o \tag{4.6}$$

Using this result, rewriting the matrix of orbital energies, ε, to the Fock matrix in AO basis, and rewriting the coefficient matrices to density matrices, the result is equation 4.7.

$$E^{(1)} = \text{Tr}[2\mathbf{DFDS^{(1)}} + 2\mathbf{Dh}^{(1)} + \mathbf{DG^{(1)}(D)}] + h_{nuc} \tag{4.7}$$

which does not depend on the derivatives of the MO coefficients.

4.2   Geometry optimization methods for DFT

The expression for the DFT gradient is different depending on which exchange-correlation functional is chosen. How these are derived will not be the focus of this thesis. The starting point, is given in equation 4.8.

$$E_{KS}^{(1)} = 2\text{Tr}[(\mathbf{Dh})^{(1)}] + \text{Tr}[(\mathbf{DJ})^{(1)}] + E_{XC}^{(1)} \tag{4.8}$$

A possible gradient for DFT was proposed by Pople and coworkers[30]. Importantly, the gradient is dependent on the derivative of the exchange-correlation term, so no one DFT gradient is known. It is closely related to the Hartree-Fock gradient.

5 Discussion

The discussion in this thesis is mostly based on the benchmarking study by Brémond et al., where 62 exchange-correlation functionals (ECFs), including four HF and post-HF methods, were tested on two different datasets; CCse21, which is a set of 21 small organic molecules, and B3se47, which is the same set, extended with 26 more small to medium sized organic molecules[1]. Equilibrium geometries were found using the aug-cc-pVTZ basis set, and the results are given as mean absolute deviations (MAD) from the reference geometry for the distance matrix.

5.1 Challenges for Hartree-Fock theory

In this section, the most significant HF challenges will be discussed. Because Hartree-Fock is a variational method, improving the wavefunctions will yield an energy that is closer to the true ground-state energy of the system[6]. When the HF energy is as close as possible to the energy from the variational principle, the Hartree-Fock limit is reached. To increase accuracy of the wavefunctions, one can increase the amount of basis functions[35]. These dictate which atomic orbitals will be included in the calculations, as well as what shape the mathematical functions have. In principle, the Hartree-Fock limit can be reached if one uses an infinite basis set. This is however not possible in practice, which means the HF wavefunction will always be an approximation, yielding some intrinsic error, which also influence post-HF methods.

The ignorance towards electron correlation in Hartree-Fock is its largest source of error[6]. Electron correlation is defined as the difference between the Hartree-Fock energy calculated at the HF limit, and the exact energy from the Schrödinger equation. While HF is about 98-99 % accurate. The remaining 1 % describes almost all chemically interesting results, like dispersion and dissociation. Because of this missing energy, the HF ground state energy will never reach the exact value. Using a post-HF method would offset this error by some value dependent on the specific electron correlation model. These could be Møller-Plesset perturbation theory (MPPT), configuration interaction (CI) or coupled cluster (CC). Both CI and CC are based on linear combinations of excited state wavefunctions, where full configuration interaction (FCI) includes all excited states of the HF Slater determinant, Φ_{HF}. FCI is the exact solution of the Schrödinger equation within a given basis set, which is too computationally demanding for most systems, but can be solved for the hydrogen molecule, for example[36]. As FCI is based on a HF calculation, basis set truncation error influences the FCI solution, and this will not be the exact solution in practice.

Hartree-Fock is usually a good approximation at equilibrium distances. This means it is a pretty accurate method for geometry optimization. However, it tends to underestimate bond lengths, as effects of bonding orbitals are overestimated[35;10]. For transition states, for example, HF struggles more. Here, there

tends to be overlapping or near-overlapping potential energy surfaces, leading to the wavefunction having large character from multiple Slater determinants. At these instances, multireference methods can be used, like complete active space CI (CASCI) or complete active space SCF (CASSCF).

5.2   Challenges for Density Functional Theory

The biggest, fundamental difference between density functional theory and Hartree-Fock is that DFT uses the electron density, whereas HF uses the wavefunctions. Because of this, one needs to know how properties depend on the electron densities[35]. However, even if one knew the exact electron density and how it affects electronic properties, the exact exchange-correlation functional is still not currently known, which causes DFT to heavily rely on approximations and empirical data. This also means that while the way to exact solution to the Schrödinger equation for HF is known (FCI with an infinite basis set), one cannot say the same for DFT.

For DFT, the Kohn-Sham orbitals are constructed. These are similar to the Hartree-Fock orbitals. One key difference lies in the external potential and how it handles occupied and virtual orbitals[35]. For DFT, all KS orbitals experience the same external potential, whereas in HF, the virtual orbitals experience a potential equivalent to adding an extra electron to the system. This leads to the virtual HF orbitals being too high in energy. There however is some debate on how useful the KS wavefunction is. The KS Slater determinant, like the HF Slater determinant (eq. 2.3), can constructed from the KS orbitals, yielding the wavefunction for a non-interacting system. This has some improvement of certain properties, but is not the main focus of this thesis.

Because the different density functional methods only differ in their ECFs, the quality of the method can be determined from the quality of the electron correlation functional. Because of this, only the ECFs need to be discussed.

It is important to note that DFT is a semiempirical method, meaning that it combines ab initio methods and empirical data in the ECFs. This means that although the ECFs discussed might yield inaccurate results for equilibrium geometries in one class of molecules, it could be more accurate for another group. In addition, ECFs are often constructed for a specific use. A big challenge for DFT is thus finding an ECF that is generally satisfactory, both for a large number of systems and for many different properties. Many studies have focused on the search for a universal ECF, including one by Peverati and Truhlar[37]. In an article by Medvedev and co-workers, it is pointed out that modern work with DFT has been too focused on empirical fitting of data, and not on the work towards universality[18].

At this time, no universal ECF has been proposed[38]. In an article by Verma and Truhlar, 15 different ECFs were benchmarked for geometries using three different databases[39]. They found that while M06-2X was one of the best ECF tested

for light-atom molecules (the DGL6 database[37]) with a mean unsigned error (MUE) of 0.004 Å, it was the worst performing ECF for transition-metal dimers (the TMDBL10 database[40]) with an MUE of 0.163 Å. They also found that PBE was the best performing ECF for the transition-metal dimers (MUE of 0.043 Å) and the worst for the light-atom molecules (MUE of 0.0013 Å). Note that the MUEs are much larger for the transition-metal dimers than for the light-atom molecules. The same ECFs were also tested for transition-states (the TSG48 database[41]), which showed similar results as for the light-atom molecules, but much higher MUEs (0.017 Å for M06-2X and 0.141 Å for PBE). This illustrates that even within the context of equilibrium geometries, no one ECF can show results to the same level of accuracy for all systems. It is further illustrated by comparing with the study by Brémond et al., where M05 showed better results than M06-2X, even though this was only of medium quality in the study by Verma et al[1].

DFT also has some general weaknesses. The most important weakness for DFT is self-interaction error (SIE)[39;42], which arises because each electron experiences a potential field from all electrons in the system. This means that each electron interacts, not only with the other electrons in the molecule, but also itself. This comes from the Coulomb potential in a one-electron system. For HF, the self-interaction part of the Coulomb potential is canceled by the exact exchange. This is not the case for DFT, as exchange is included in the ECF, which is only an approximation. SIE also leads to delocalisation error. How this arises is explained by Li et al.[42], but will not be explained further here. The consequences of delocalisation error is that the electron densities of most systems are predicted to be too spread out, which causes the energies the be lowered, unphysically.

In general, DFT also struggles with dispersion and hydrogen bonds[39]. These are electron-correlation problems, which means they are poorly described by HF as well, in practice HF is in fact incapable of modeling this interaction. Because of this, multiple empirical dispersion-corrected functionals have been proposed for DFT[43]. These are needed to describe weakly bonded systems, which is important for biochemistry, and are essential for interactions between closed-shell species. According to the Hohenberg-Kohn theorem, properly dispersion corrected ECFs should exist, and the issues are possibly purely mathematical[6]. When dispersion is improperly described, equilibrium structures for Van der Waals complexes are distorted, and larger structures get wrongly calculated energetic properties. Double hybrids have been proposed as an alternative to dispersion corrected ECFs. For more information on specific dispersion corrected ECFs, see the study by Grimme[43]. For hydrogen bonding, most ECFs predict them to be too short, compared to real systems. For HF these tend to be surprisingly good, because the of a cancellation of error between covalent character (too tightly bound) and dispersion character (too weakly bound).

5.3   Comparing the exchange correlation functionals

Brémond et al. found that HF showed deviations of 0.0250 (HNCCN$^+$) to 0.0054 (CH$_2$ClF) Å, with a MAD of 0.016 Å, for the distance matrices of the CCse21 set[1]. For this dataset, HF was the worst-performing method out of all the methods tested. For B3se21, it was better than the BLYP ECF, and equal to PBE. Looking specifically at the CH-, CC-, and CO-bonds in the CCse21 set, the CO-bonds proved most challenging for HF, while the CC and CH-bonds were close to the errors for the worst performing ECFs. In another study, Johnson et al. found that the mean deviation for HF bond lengths was -0.010 Å at equilibrium geometries for a group of molecules made up of second row atoms[44]. Both these studies illustrate that HF systematically underestimates bond lengths, which fits theory.

Using electron correlation models should improve the HF geometries. For Johnson et al., the most accurate results were found using MP2 (MPPT to the second order correction)[44]. For Brémond et al, MP2 was only beaten by 10 ECFs for the B3se47 set and 19 for the CCse21 set, where four of these were ab initio DFT methods[45;46;47;48;49;50;51]. According to DeFrees et. al.[52], MP2 showed improved results for both AH and AB bond lengths, where A and B are atoms heavier than hydrogen. Lucchese et al.[53] however, found that the bond lengths for fluorine peroxide (F$_2$O$_2$) were not significantly improved by electron correlation methods. According to Amos and coworkers, MP2 for F$_2$O$_2$ is very dependent on the basis set, but should yield better results than HF[54]. They also found that the ECFs tested gave better results than SCF methods, except for CCSD(T) with a large basis set.

Of the ECFs, the worst performing functionals were the non-hybrids, or local ECFs. For the B3se47 set, some of these methods had larger MADs than HF. The results show that SVWN, which is an LDA, did not necessarily do worse than other locals. This is surprising, as LDA is one of the most primitive ECFs. The two dispersion corrected local ECFs, B97D and B97D3 did not do much better than the non-dispersion corrected locals. This is not surprising, as the molecules tested were single organic molecules, small enough to be relatively independent of dispersion effects. For bigger biochemical systems, this would be much more important, and the dispersion-corrected ECFs would most likely outperform ECFs of the same type. The best performing local ECF was M06-L. While it is unexpected that a local performs better than many hybrids, what is more surprising is that M06-L was not made for calculating geometries[55]. In addition, local ECFs usually perform better for metals, where electrons behave more like the uniform electron gas model that DFT was based on.

The best performing functionals were the double hybrids, dominated by the ECF xDH-PBE0. Of the 12 double hybrid functionals tested, nine were in the top ten best performing ECFs for the CCse21 set, and seven for the B3se47 set. Only one of the three ab initio double hybrids performed better than MP2, however[47]. It is no surprise that double hybrid functionals perform well, as they include contri-

butions from MP2 and other MP2-like methods, not just HF. For mathematical discussions on the double hybrids, see Martin and Santra (2019)[56]. Double hybrids have been found to give very good results for large, diverse databases, seemingly approaching universality. The biggest problem with double hybrids is static correlation, which means transition metal systems are badly described. However, the MP2-like contribution to the correlation means this is improved somewhat from semilocal ECFs. Static correlation might be what causes the MAD values of the double hybrids. A solution of this could be to use a multiref-erence method. Martin and Santra also point out that singlet-paired CC could improve results.

Of the global hybrids, those including more than 40 % of the exact exchange (EXX) from HF did better overall than those with less than 40 % EXX. Many of these were on the same level as MP2. The accuracy of global hybrids with less than 40 % EXX do not show a clear trend. The best global hybrid was SOGGA11-X (>40 % EXX), which was almost on the level of the double hybrids. That means SOGGA11-X might be a good alternative when post-HF methods, and thus double hybrids, are unavailable.

Over the last few years, range-separated functionals have been introduced. These can be combined with hybrid, double hybrid or semilocal ECFs. For the study by Brémond et al, the double hybrids showed better results than the range sepa-rated hybrids, but they showed no general improvements to the global hybrids[1]. However, range separated schemes show great promise in general, and can solve problems where the other ECFs fail. An example of this is the structure of an sp-hybridized carbon allotrope, with alternating single and triple bonds[57]. This study showed that only the range-separated schemes were able to predict the correct geometry.

Now that the results of different ECFs have been discussed, it is important to also look at the computational cost and time. This varies, depending on what program one uses. Formally, DFT methods scale as N^4, meaning that if the number of atoms increase by N, the runtime increases by N^4. This has been reduced to N^3 through density fitting[29]. Programs that are designed for DFT calculations often implement this. In these programs, the cost of HF and DFT are about the same, but DFT often yields better results. This is of course dependent on what ECF is used as well. For programs designed for HF, the scaling of DFT is the same as HF (N^4), but the cost of the DFT calculations are about double that for HF[35]. DFT reaches basis set convergence faster than HF and post-HF methods do, and can thus do calculations with smaller basis sets, yielding better results. One problem for DFT is that the KS orbitals converge slower than HF orbitals in an SCF scheme. This can however be solved by using the optimized HF orbitals as an initial guess for the KS orbitals, but then a HF calculation needs to be done before the DFT calculation.

For post-HF methods, MP2 scales as N^5 and CCSD(T), which is considered to be a very accurate method[58], scales as N^{7}[35]. For different ECFs the scaling is

the same, but local ECFs are generally faster than non-local methods[55], which makes sense, considering the HF contribution that needs to be added. According to Yu and coworkers, the cost of LDA methods is not significantly lower than that of GGAs or mGGAs[59]. It is however reasonable to assume that GGA and mGGA calculations are somewhat slower than LDA calculations, as their functionals include the gradient, as shown in equations 3.23 and 3.24. See Ekström et al. for more discussion on this[60]. According to Martin and Santra, the inclusion of MP2 in double hybrid functionals is of little importance in terms of scaling[56]. Calculations take about as long as other hybrid ECFs, assuming MP2 is available in the program used. In a paper by Zhao and coworkers however, they claim the double hybrid methods are much more computationally demanding (and thus expensive) for DH methods than for other hybrid methods[61].

Concluding remarks

A benchmarking paper by Brémond et al. was used as basis of discussion for geometry optimization with Hartree-Fock, MP2 and 59 ECFs. The results of this paper showed that double hybrid functionals did best overall, with xDH-PBE0 being the best performing functional. The global hybrids with more than 40 % contribution from Hartree-Fock did better than those with less EXX. Of the global hybrids, SOGGA11-X performed best. The local ECFs did worst of the DFT methods, but M06-L did surprisingly well. Hartree-Fock did worst overall, systematically underestimating the bond lengths, but beat BLYP for the bigger set of molecules. It was also found that using MP2 improved the results, but it was still not on the same level of precision as the bulk of the double hybrids. Range separated hybrids showed no clear trend in this study, but are known to do well in areas where other ECFs struggle.

The results are seen in light of the empirical fitting of ECFs, and how they are designed for a specific purpose. It seems like the double hybrids are approaching a point of universiality, but from the results it is apparent that they are not the exact solution to the Schrödinger equation. The search for an ab initio universal ECF with high precision should continue in the coming years, as empirical ECFs currently show the best results.

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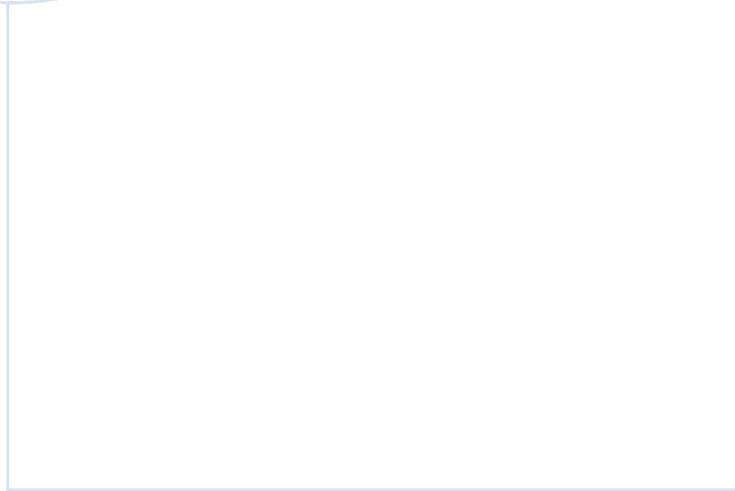
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