On the Use of a Dual Mean Field Approach for DFT+NEGF Electronic Transport Modelling

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This thesis focuses on electronic transport modelling in molecular junctions. The most common technique for modelling electron transport is the combination of Density Functional Theory (DFT) and Non-Equilibrium Green's Function's (NEGF). Conventional DFT+NEGF methods are, however, invalid for correctly modelling junctions under a bias voltage.

In 2015 Liu et al [1, 2] have proposed a Dual Mean Field (DMF) extension to DFT+NEGF that enables the correct modelling of non-equilibrium systems. In contrast to the conventional DFT method, the DMF approach utilises two electron density fields to correctly account for the bias-induced non-equilibrium effects. This research has implemented the proposed DMF in the existent BAND software of SCM. The thesis intends to motivate further development of the DMF method.

Electron transport calculations are performed using a DMF adapted LDA exchange-correlation functional in a 3x3 Al-BDA-Al junction. The results are compared to calculations with a conventional VWN LDA XC functional. The DMF approach leads to a 20% mean increase in the HOMO-LUMO gap. This is an important and promising result, as conventional LDA methods are known to underestimate the HOMO-LUMO gap. Additionally the bias dependence of the transmission spectrum has been analysed. This yields similarly good stability as the conventional LDA method.

These first results encourage additional testing and development of the DMF method. Next steps are the incorporation of relativistic effects and the implementation of more advanced XC functionals.
In September 2017 I started working on this research. I would like to take a brief moment to thank the people who have supported me.

First I would like to thank Nikolas Kavadias, José Arturo Celis Gil and Pier Philipsen. Nikolas for his introduction to the BAND software, José for his numerous tips and tricks on running calculations, and thirdly Pier, one of the main developers of BAND, for providing valuable insights in the BAND code throughout the year.

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Thirdly I would like to express my gratitude towards Jos Thijssen, my primary supervisor. Together we started the project, and at the time we did not know how far we would come. I am pleased with the progress we have booked, and admit this is largely due to the weekly sessions Jos and I have had. These fruitful discussions have led to the most essential insights for the implementation. Additionally, Jos’ sheer knowledge in the field of molecular electronics has been a perfect mirror for evaluating my own understanding.
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### Abbreviations

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<tr>
<td>AO</td>
<td>Atomic Orbital</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>DMF</td>
<td>Dual Mean Field</td>
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<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<tr>
<td>HK</td>
<td>Hohenberg-Kohn</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<td>KS</td>
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<td>LDA</td>
<td>Local Density Approximation</td>
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<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
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<td>NEGF</td>
<td>Non-Equilibrium Green’s Function</td>
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<tr>
<td>SCF</td>
<td>Self-Consistent Field</td>
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<td>SE</td>
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In 1965 Gordon Moore described his famous Moore’s law: the number of transistors on a chip doubles approximately every two years. Fifty years down the road this law still holds. In a technological society that keeps demanding larger computation power, there is a strong motivation to keep this trend alive. The most obvious way to do so is to decrease the transistor size even further, until we have arrived at the realm of molecules. Scientists are not yet up for this task, for a lot of physics still needs to be discovered about this very small world.

In my bachelor thesis I have focused on one particular part of the molecular world: a molecular junction. This research aims to model electronic transport in these very small structures, with the purpose of acquiring more effective tools to model small structures in general. Experimental research in this field is being conducted, but as of today this is technically difficult and tends to yield inconsistent results. It is therefore important to compare theory and experiment. As electrical currents are easily measured, it is natural to focus research on current.
Knowledge of electronic behaviour on this scale is essential for miniaturizing electronics. The research in this thesis intends to give insight into this area of physics. In this work we use BAND software from SCM[3, 4, 5, 6, 7, 8]. In standard electron transport calculations, a non-equilibrium Green's function (NEGF) is used in combination with density functional theory (DFT). In 2015, Liu et al[1] have proposed an extension to this paradigm. In this thesis we have implemented Liu's idea in the BAND software.

Chapter 2 introduces the concept of a molecular junction. In Chapter 3 a theoretical framework is laid down for modelling transport in such a set-up, using the conventional modelling techniques already existent in the BAND software. Chapter 4 introduces Liu's dual mean field method and its implementation in BAND. This implementation is elementary, but may provide a proof of concept for further development. Chapter 5 contains the modelling results that follow from the new implementation, and compares these to the conventional DFT+NEGF method of BAND. The final chapter concludes and offers promising directions for further research.
Let us first introduce molecular junctions. A molecular junction generally consists of two semi-infinite regions of conducting material, with a molecule or other structure in between. The conducting regions are called the leads. The combination of molecule and lead contacts is called the extended molecule or device, see Figure 2.0.1. In the case of transport calculations, a small voltage\(^1\) is applied on the leads. This means the chemical potential in the left and right lead is different.\(^2\) Electrons will be transferred from one lead to the other lead, called the source and drain respectively. This research focuses on \textit{ab initio} modelling of the junction. In this approach, a theoretical method is used that models a molecular junction, given only an atomic set-up and bias voltage.

\(^1\)Usually in the range of mV up to a few hundred mV
\(^2\)Without loss of generality, in this research we assume the left lead has a higher potential than the right lead.
Figure 2.0.1: Computer rendered image of a molecular junction consisting of a 1,4-benzene-di-amine (BDA) molecule and two golden leads. The green and red atoms are the regions of the extended molecule that belong to the leads.
One might also be interested to look at the energy levels of the junction. Because the leads are conducting these are assumed to be in equilibrium, with the energy bands filled up to the chemical potential $\mu_L$ and $\mu_R$ for respectively the left and right lead. Coupling of the device and leads results in a flow of electrons (or holes) from one lead to the other. These moving electrons constitute a current.

Inside the device electrons can occupy molecular states. In this experiment, we assume (near) zero temperature. No thermal excitations are present and electrons are found only in the least energetic states. Noteworthy are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The gap between these two states will be a useful quantity, as will become clear in Chapter 5.

For an uncoupled device, its states have a single energy. Coupling to the leads causes a broadening of these energy peaks. The stronger the coupling, the wider the peak becomes. States inside the device are filled to somewhere in-between the chemical potential of both leads. The current through the device is determined by the available states that, in terms of energy, lie between the potentials of the leads; the so-called bias window. A larger bias means more states lie in the bias window, hence more states are available for electron transport. The most characteristic quantity for electron transport is therefore the transmission spectrum of a device: a device’s ability to conduct current at a certain energy level.

The next chapter describes a theoretical framework to model a junction, which ultimately leads to expressions for, inter alia, a junction’s transmission spectrum.

---

3 This can be explained by the uncertainty principle. If the device is strongly bound, electrons can easily escape the device. The time an electron resides on the molecule therefore decreases with increased coupling. Consequently, the uncertainty in energy $\delta E = \hbar/\delta t$ becomes larger: the peaks widen. [9]
Molecular junctions are at most a few nanometers in size, hence these systems require a quantum mechanical description. The usual start for understanding the system is therefore the Schrödinger equation. This research aims at predicting the properties of a junction, which in principle can be calculated by the Schrödinger equation alone. This, however, comprises solving a Hamiltonian that involves multiple interacting particles. The resulting implicit equation is practically impossible to solve exactly or computationally. Modelling a molecular junction therefore demands for multiple approximations.

The software that the current work uses is SCM BAND, which is based on the Born-Oppenheimer approximation, Density Functional Theory (DFT) and Non-Equilibrium Green’s Functions (NEGF).

This chapter describes how molecular junctions can be modelled mathematically. It starts of with the difficulty of the Schrödinger equation, subsequently it summarizes the
Born-Oppenheimer approximation and lastly sketches a rough workings of DFT and NEGF.

3.1 **FORMALISM**

Let us first take a look at the general formalism for modelling a quantum mechanical system of particles. All information of the molecular device is contained in the solution of the Schrödinger equation, $\hat{H}\Phi = i\hbar \frac{\partial}{\partial t} \Phi$. The solution is the wave function $\Phi$ - the system's state - that describes the behaviour of all particles within the system. The Hamiltonian $\hat{H}$ is the quantum mechanical energy operator that plays a dominant role in understanding a quantum system like ours. Let us therefore take a closer look at the Hamiltonian $\hat{H}$ of the system.

3.1.1 **HAMILTONIAN**

The Hamiltonian includes the different particles of the system. It includes the kinetic energy operator for electrons and nuclei, the Coulomb interaction and an external potential. The particles at hand are electrons and nuclei. This gives:

$$
\hat{H}_{\text{tot}} = \sum_i \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{|r_i - r_j|} + V_{\text{ext}}(r_i) \right] + \\
+ \sum_l \left[ -\frac{\hbar^2}{2M_I} \nabla_l^2 + \frac{1}{2} \sum_{j \neq l} \frac{Z_I e^2}{|R_l - R_j|} + V_{\text{ext}}(R_l) \right] - \sum_{i} \sum_{l} \frac{Z_i e^2}{|r_i - R_l|},
$$

(3.1)

in which the first line represents the energy of electrons, the second of the nuclei and the third represents Coulomb attraction between electrons and nuclei. Within the large sums, the first term is the kinetic energy, the second the Coulomb repulsion and the third the external potential. Note that $\nabla_i(\cdot)$ operates on electron (nucleus) $i(\cdot)$, $m_e(M_i)$ is the electron (nuclear) mass, $e$ is the elementary charge, $Z_I$ denotes the atomic number (hence charge) of nucleus $I$ and $V_{\text{ext}}$ refers to an externally applied potential. Note that the electron-electron Coulomb term and nuclei-nuclei Coulomb term count every pair twice, hence the one-half in front of the sums.
3.1.2 Born-Oppenheimer Approximation

Electrons are much faster than nuclei, hence on the timescale of electronic transport, the motion of nuclei can be disregarded. The interaction of the nuclei with the electrons is approximated as a static external potential field working on the electrons. This is called the Born-Oppenheimer approximation and leads to the electronic Hamiltonian:

$$\hat{H}_e = \sum_i \left[ -\frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_{j \neq i} \frac{1}{|r_i - r_j|} + \tilde{V}_{\text{ext}}(r_i) \right],$$  \hspace{1cm} (3.2)

where we have switched to atomic units.\(^1\) Note that the first term is still the kinetic energy, the second the Coulomb repulsion and the third, the external potential \(\tilde{V}_{\text{ext}}\), includes the static potential originating from the nuclei.\(^2\) From now on, we will drop the tilde.

This Hamiltonian contains an ‘easy’ and a ‘difficult’ part: one part that only depends on single, independent electrons and one part that depends on all other electrons too. The Hamiltonian can therefore be split into the single-electron Hamiltonian and the interaction Hamiltonian.

$$\hat{H}_{se} = V_{\text{ext}}(r_i) - \frac{1}{2} \nabla_i^2,$$  \hspace{1cm} (3.3)

$$\hat{H}_{\text{int}} = \frac{1}{2} \sum_{j \neq i} \frac{1}{|r_i - r_j|}.$$  \hspace{1cm} (3.4)

The interparticle dependency within the interaction term prohibits a separated calculation of individual electron states, making the calculations implicit. For \(N\) electrons this leads to a \(3N\) dimensional problem. In Appendix A this difficulty is illustrated. The high dimensionality of the problem urges the use of Density Functional Theory (DFT).

---

\(^1\) Atomic units use \(\hbar = 2m_e = e = 4\pi\varepsilon_0 = 1\). The atomic unit of energy is Hartree, which is approximately 27.211 eV. Unless stated otherwise this work uses atomic units.

\(^2\) The Coulomb attraction leads to singularities at every nucleus. Calculating the new external potential by numerical integration is therefore not as straightforward as one might think. A Becke grid is used to allow spherical integration \([6, 10]\).
3.2 DFT

It is incredibly difficult to find an eigenstate $\Phi$ of the Hamiltonian in Eq. 3.2, because of the high dimensionality of the problem; a lot of dependent particles are involved. The dimensionality can be dramatically decreased by reformulating the problem using DFT.

3.2.1 Electron Density

Density Functional Theory (DFT) benefits from the fact that it is not the individual electron behaviour we are after, but the general electron behaviour. DFT is based on the two Hohenberg-Kohn (HK) Theorems. These theorems dictate the following:

1. The external potential $V_{\text{ext}}(r)$ is determined, within a trivial additive constant, by the ground-state electron density $n_0(r)$. Consequently, all properties of the system are governed by the Hamiltonian and completely determined by the ground-state density $n_0(r)$.

2. A functional $E[n(r)]$ exists for the energy, such that the global minimum of this functional equals the ground-state density $n_0(r)$.

It introduces a property called the electron density, which is formally defined as follows:

$$n(r) = \sum_i |\varphi_i(r)|^2; \quad (3.5)$$

where the sum is over the occupied normalized orbitals (see Appendix A). The equation describes the expected number of electrons to be present at a certain $r$ by simply summing over the probabilities of finding an electron in a particular orbital at $r$.

The first theorem essentially asserts that if one knows the electron density $n(r)$ of a system, all system properties can be derived using the Hamiltonian. The second theorem claims that a functional exists such that the minimum of this functional is exactly the ground-state energy. This minimum is assumed for the exact ground-state density. Using the electron density as a central

\footnote{i.e. because potentials are defined in respect to a reference point. Nonetheless, this does mean the entire system should be measured with respect to the same reference point. A so-called alignment run is needed to align these reference energies. A thorough explanation is given by Verzijl\[12\].}
quantity implies a tremendous reduction of the complexity, as the wave function, which is a function of \(3N\) coordinates, is replaced by the density, which is a three-dimensional function. The single-particle orbitals from which the density can be constructed are found as the solutions to the Kohn-Sham Hamiltonian: [13]

\[
\hat{H}^{KS} = -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{\text{XC}}[n](\mathbf{r})
\]

\[
= T + V_{\text{ext}}(\mathbf{r}) + V_H[n](\mathbf{r}) + V_{\text{XC}}[n](\mathbf{r}),
\]

(3.6)

with \(T\) the kinetic term, the interaction, or Hartree, potential \(V_H\), the external potential and \(V_{\text{XC}}\) the exchange-correlation potential. As the name suggests, the latter includes both exchange and correlation effects. Exchange interaction is the result of the fermionic nature of electrons. The correlation potential is a correction to the Hartree term.\(^4\)

The simplicity of the interaction term is the appeal of DFT. However, the exchange-correlation term is less pleasing. The second HK theorem states that an exact functional exists for \(E_{\text{XC}}\), but the exact form of this functional is unknown. [14] The exchange-correlation functional should hence be approximated. The easiest method to do so is a Local Density Approximation (LDA). This method is used in this work and described in detail in Appendix B.

### 3.2.2 An outlook on Self-consistent Field Theory

At this point the DFT Hamiltonian is still implicit: without knowing the state of the system, the electronic density cannot be calculated. However, DFT enables the use of a self-consistent method.

Self-consistent field theory (SCF) is an iterative process that seeks for a stationary solution.\(^5\) Given an electron density \(n(\mathbf{r})\), the Hamiltonian is calculated. Subsequently, the non-interacting single-electron Equation 3.6 can be solved. From its solution a new density \(n(\mathbf{r})\) is calculated and the process repeats until convergence. Visualised:

\[
n^0 \rightarrow H \rightarrow \Phi \rightarrow n^1 \rightarrow ...
\]

\(^4\)Both are explained in-depth in Appendix B

\(^5\)Because the lowest energy state is the most stable state, the stationary solution corresponds to the ground-state electron density \(n(\mathbf{r})\) from the HK theorems.
The SCF method will be further elaborated on in Section 3.4.

This section has covered the calculation of $H$ given electron density $n$. The next section describes how the new density $n(r)$ can be found in a non-equilibrium system.

3.3 NEGF

Given the DFT approach above, we would like to find the new electron density. To do so, Non-Equilibrium Green’s Functions (NEGF) are used. Hitherto we have sketched a general picture of how an equilibrium quantum device can be modelled. From now on the specific case of a transport device is used.

The electron density is constructed as a linear combination within a basis set of three dimensional functions. A basis set consisting of numerical atomic orbitals (NAO’s) $\{\chi_i\}$ is chosen. The set consists of multiple NAO’s centered at each atom in the set-up. The size of the basis set has major impact on both the accuracy and the computing time. In Appendix C this set is motivated and further explained.

The functions are partitioned according to their location and put into a vector:

$$\chi = \begin{bmatrix} \chi_L \\ \chi_D \\ \chi_R \end{bmatrix},$$

such that $\chi_L$ denotes the orbitals in the left lead and $\chi_D$ are orbitals in the device region. Note that a finite number of orbitals are included for every nucleus, but because the number of nuclei in the leads is infinite the $\chi_{L(R)}$ are infinite too.

Next the Fock matrix $H$ is defined. This is the matrix form of the Hamiltonian of Eq. 3.6 expressed in terms of the AO basis functions. Entry $H_{ij} = \langle \chi_j \mid \hat{H} \mid \chi_i \rangle$. The Hamiltonian matrix can be partitioned as follows:

$$H_{tot} = \begin{pmatrix} H_L & \tau_L^\dagger \\ \tau_L & H_D & \tau_R^\dagger \\ \tau_R & H_R \end{pmatrix}, \quad (3.7)$$
where $H_D$ denotes the submatrix of states within the device, likewise $H_{L(R)}$ the left (right) lead and $\tau_{L(R)}$ the hopping term: the coupling of states within the left (right) lead to the states in the device. Because the leads are semi-infinite and periodic, the Hamiltonians $H_{L(R)}$ can be found using Bloch’s theorem on the bulk leads.\footnote{Because the leads are taken to be semi-infinite, the matrix $H_{tot}$ is infinite too. This, in addition to the junction’s non-periodicity, causes the Hamiltonian to be unmanageable.}

Because the leads are taken to be semi-infinite, the matrix $H_{tot}$ is infinite too. This, in addition to the junction’s non-periodicity, causes the Hamiltonian to be unmanageable.

The Non-Equilibrium Green’s Function (NEGF) method circumvents this problem by introducing the Green’s matrix of the Hamiltonian. In quantum physics, the Green’s function, or in this case matrix, is a propagator: it expresses the probability of an electron’s state evolving from one orbital to another.\footnote{The quantum mechanical Green’s function is conceptually different than the Green’s function used for studying differential equations, where it is defined as a system’s impulse response. See \cite{14} or \cite{16} for exhaustive derivations and comparisons.}

Following Stokbro\footnote{We do not necessarily require the basis to be orthonormal, hence this definition. If the basis is orthonormal, $S$ would just be the identity matrix, simplifying the Green’s function’s definition. \cite{15} explains the need to include $S$ in Eq. 3.8.}, the Green’s matrix $G$ as a function of energy $E$ is defined by:

$$\begin{align*}
(E\mathbf{S} - H_{tot})G(E) &= \mathbf{I}, \\
\begin{pmatrix}
E\mathbf{S}_L - H_L & E\mathbf{S}_{L\tau} - \tau_L^\dagger \\
E\mathbf{S}_{\tau L} - \tau_L & E\mathbf{S}_D - H_D & E\mathbf{S}_{\tau R} - \tau_R^\dagger \\
E\mathbf{S}_{\tau R} - \tau_R & E\mathbf{S}_R - H_R
\end{pmatrix}
\begin{pmatrix}
G_L & G_{L\dagger} \\
G_{LD} & G_D & G_{RD} \\
G_{RD} & G_R
\end{pmatrix} &= \mathbf{I}
\end{align*}$$

(3.8)

where $S$ is the overlap matrix of the chosen basis:\footnote{This is largely due to screening by the contacts: orbitals within the device and the bulk of metal do not ‘see’ each other, because of the metallic contact that is in between.}

$$S_{ij} = \langle \chi_j | \chi_i \rangle.$$  \hfill (3.9)

The switch to the Green’s function allows us to focus on the part of the Hamiltonian that we find interesting: the device region. Key are the submatrices $\tau$ in Eq. 3.7. Although the leads are infinite, there are only a few atomic orbitals in the leads that couple to the device:\footnote{This is largely due to screening by the contacts: orbitals within the device and the bulk of metal do not ‘see’ each other, because of the metallic contact that is in between.}
close to the device. Consequently, the matrix $\tau$ is empty except for a few entries near the lead-device interface. To understand how this helps us, we can extract from Eq. 3.8 the device’s Green’s function:

$$G_D(E) = (ES - H_D - \Sigma_L - \Sigma_R)^{-1}, \quad (3.10)$$

with the self-energy $\Sigma_{L(R)}$ defined by:

$$\Sigma_{L(R)} = (ES_{\tau_L(R)} - \tau_{L(R)^\dagger})(ES_{\tau_L(R)} - H_{L(R)})^{-1}(ES_{\tau_L(R)} - \tau_{L(R)}), \quad (3.11)$$

with $g_{L(R)}$ the surface Green’s function: the part of $G_{L(R)}$ that corresponds to states in the very tips of the leads. The surface Green’s functions can be calculated from leads’ Hamiltonians, using an efficient recursive algorithm $[17],[18]$.

In quantum mechanics, non-Hermitian operators describe nonconserved quantities. The non-Hermitian part of the self-energy $\Sigma$ is related to transport: this allows particles to enter or exit the system. We define the coupling $\Gamma$ by:

$$\Gamma_{L(R)}(E) = -2\Im\{\Sigma_{L(R)}(E)\}. \quad (3.12)$$

The electron density matrix is obtained from the Green’s function as: $[12]$

$$\rho = \frac{1}{2\pi} \int_{-\infty}^{\infty} \left[ G_L \Gamma \Gamma_R^\dagger f(E, \mu_L) + G_R \Gamma \Gamma_L^\dagger f(E, \mu_R) \right] dE, \quad (3.13)$$

with $f(E, \mu)$ the Fermi-Dirac distribution. The Fermi-Dirac distributions provide a smooth cut-off at the left and right lead’s potential. This matrix describes to what extent every orbital in the basis set is occupied. Integration is performed numerically.

Ultimately we would like to know the spatial electron density. The density $n(r)$ can be found by a simple sum:

$$n(r) = \sum_{i,j} \chi_i(r) \Re\{\rho_{i,j}\} \chi_j(r), \quad (3.14)$$

after which the SCF loop can be restarted again. Let us conclude by taking a bird’s eye view on the SCF scheme.
3.4 SCF

The use of DFT facilitated an easy expression for the Hamiltonian by introducing the electron density. The use of Green’s functions subsequently enables finding this electron density, given a Hamiltonian matrix. Together these allow Self-consistent Field Theory to be used. The earlier described SCF loop is extended to the following scheme:

\[ n^{(0)} \rightarrow H + \Sigma_L + \Sigma_R \rightarrow G \rightarrow n^{(1)} \rightarrow \ldots \]

until convergence is reached.\(^9\)

In this loop, the density used for loop \((n + 1)\) is not just the density that resulted from loop \(n\): it is a linear combination of multiple prior densities. The procedure that judiciously guesses a new density is called Direct Inversion of the Interative Subspace (DIIS). DIIS is an extrapolation technique most often used for self-consistent loops in chemical calculations. The technique predicts a new density based on the errors of the previous densities. Different DIIS models are in use, BAND uses the DIIS+ADIIS method by Hu and Yang\[^{19}\].

If convergence is reached, the Meir-Wingreen equation \[^{20}\] is used to calculate the transmission of the system:

\[ T(E) = \text{Tr} \left[ \Gamma_L(E)G(E)\Gamma_R(E)G^\dagger \right], \tag{3.15} \]

in which \(\text{Tr}\) denotes the trace: the sum of the diagonal elements of the enclosed matrix. The transmission reflects the system’s capability to transmit current at a certain energy level. The current is calculated by:

\[ I = \frac{2e}{h} \int (f(E, \mu_L) - f(E, \mu_R)) T(E) dE; \tag{3.16} \]

in which the Fermi-Dirac distributions ensure the transmission is smoothly integrated over the bias window.

Other system properties, like the (local) density of states, can also be acquired from the Green’s matrix.\[^{12}\]

\[^{9}\] Convergence is not guaranteed. More on this in the chapter Discussion.
The DFT+NEGF method proposed in the previous chapter has been used and improved for many years. Nevertheless, DFT is theoretically not valid for non-equilibrium electron transport.\textsuperscript{1} This chapter discusses a dual mean field (DMF) method proposed by Liu et al\textsuperscript{[1, 2]} to remedy this problem. The chapter also includes an elementary implementation in BAND aiming to provide a proof-of-concept for further research.

4.1 DMF

DFT replaces the many-body Hamiltonian by the independent single-electron Hamiltonian. The single-electron Hamiltonian only depends on the ground-state wave function of the independent electron. This reduction is based on the Hohenberg-Kohn theorems \textsuperscript{[11]}.

\textsuperscript{1}This is a result of the Hohenberger-Kohn theorems, the justification of DFT. More on this in the next section.
These theorems are valid for the ground-state of a system. In non-equilibrium ‘ground-state’ has no meaning and instead we focus on a steady state solution. In theory non-equilibrium steady-state electron transport can be achieved by using an adiabatic time evolution of the system. An adiabatic evolution is infinitesimally slow and proper approximations are thus computationally unfeasible. The conventional implementation inserts the molecule between two leads that are individually in equilibrium, after which it uses the SCF loop to reach a stationary density.

The necessity of adiabatic evolution can be avoided using a theory developed by Hershfield [21]. Liu et al [1, 2] have applied this theory to the case of molecular electron transport. This method uses a dual mean field (DMF) approach: it uses not one but two different densities. Within the scope of this report, we do not analyse the theoretical background in detail, but restrict ourselves to a description of the method.

In contrast to conventional DFT that uses the total electron density as principle function, DMF is expressed in terms of the equilibrium and non-equilibrium densities \( n_e(r) \) and \( n_n(r) \). These are defined as:

\[
n_e(r) = \sum_i f(\epsilon_i, \mu_R) |\varphi_i^e(r)|^2, \tag{4.1}
\]

\[
n_n(r) = \sum_i [f(\epsilon_i, \mu_R) - f(\epsilon_i, \mu_L)] |\varphi_i^n(r)|^2, \tag{4.2}
\]

with \( f(E, \mu) \) the Fermi-Dirac distribution. Note that \( n_t = n_n + n_e \) is the total electron density as we used it before (see Eq. 3.5).

In the DMF approach the Hamiltonians for both densities become

\[
\hat{H}_e = -\frac{1}{2} \nabla^2 + V_{\text{ext}} + V_H[n_t] + V_{XC}, \tag{4.3}
\]

\[
\hat{H}_n = -\frac{1}{2} \nabla^2 + V_{\text{ext}} + V_H[n_t] + V_{XC}^n - \frac{V_b}{2}, \tag{4.4}
\]

with \( V_b \) the bias voltage.

---

1This comes down to starting with two regions that are individually in equilibrium at \( \mu_L \) and \( \mu_R \), but uncoupled and separated by an infinite potential barrier. Over an infinite amount of time the infinite potential barrier is removed and the systems are coupled, such that the equilibrium system becomes a non-equilibrium steady state transport system. See also [2].

---
The expression of the Hamiltonian differs in the exchange-correlation term and in the bias term. In Appendix B.2 an LDA approximation for the exchange-correlation term is given.

The Green's functions of the equilibrium and non-equilibrium densities are found using the conventional equation for both Hamiltonians (see Eq. 3.10). Although the Hamiltonians of both densities are different, the self-energies $\Sigma_{L(R)}$ of the leads influence the equilibrium and non-equilibrium densities equivalently.\(^3\)

To finish the SCF loop, an expression for the new densities is needed as a function of the Green's functions. The definition requires only equilibrium electron states to be counted for in $n_e(r)$ and non-equilibrium electron states in the energy range of the bias window to contribute to $n_n(r)$. The calculation of these therefore differ from the conventional calculation (Eq. 3.13). For the equilibrium density, both leads are assumed to be in equilibrium at $\mu_R = \varepsilon_F - \frac{V_b^2}{2}$. The density matrix of Eq. 3.13 simplifies to: \(^2, 16\)

$$\rho_e = -\frac{1}{2\pi} \int \Im \{G_e(E)\} f(E, \mu_R) dE \quad (4.5)$$

On the other hand, the non-equilibrium density only includes the part in the bias window:

$$\rho_n = \frac{1}{2\pi} \int G_n(E)\Gamma_L(E)G_n(E)^\dagger (f(E, \mu_L) - f(E, \mu_R)) dE \quad (4.6)$$

Both spatial densities $n_e$ and $n_n$ are subsequently calculated using Eq. 3.14.

The non-equilibrium density $n_n$ is the only density that contributes to transport. A summarized procedure for finding properties like the transmission or current is thus:

$$n_e^{(o)} \rightarrow H_e + \Sigma_L + \Sigma_R \rightarrow G_e \rightarrow n_e^{(o)} \rightarrow \cdots \rightarrow n_e^{(M)}$$

$$\uparrow \text{exchange interaction} \uparrow$$

$$n_n^{(o)} \rightarrow H_n + \Sigma_L + \Sigma_R \rightarrow G_n \rightarrow n_n^{(o)} \rightarrow \cdots \rightarrow n_n^{(M)} \rightarrow T(E) \rightarrow I$$

with $M$ the total number of iterations.

\(^3\)On the grounds of the leads - excluding the surface layers - being in equilibrium.
4.2 Implementation BAND

The solution proposed above has been implemented in BAND. The main adjustment is the need for two separate SCF loops to be run, which are linked in every loop by the calculation of the Hamiltonian - specifically the exchange energy. The DMF approach has been implemented with the LDA functional of Appendix B.

The integration for both density matrices (Eqs. 4.5 & 4.6) is performed numerically. This is not an easy task though, because the complex integrand can be very irregular on the real-axis. In the equilibrium case, the poles are known to be located just below the real axis of energy.\[12\] Consequently, a very large number of points would be needed to evaluate the integral on this real energy line. This integration can be performed more efficiently by integrating the complex continuation of the integrand over a different contour in the complex plane. This requires fewer integration points while maintaining accuracy. See Figure 4.2.1. Note that the Fermi-Dirac function has poles too, situated above the Fermi energy. Applying the residue theorem, the integral over the real-axis equals the residue of the enclosed Fermi poles minus the integration over the alternative contour. This is the same method used for non-biased calculations. For an exhaustive description, see [12, 22].

In the non-equilibrium equation of Eq. 4.6, the location of the poles is more difficult to predict. Because of the inclusion of both $\mathbf{G}$ and $\mathbf{G}^\dagger$ the poles are not limited to the lower half-plane. The alternative contour integration is no longer possible. A conventional integration is performed over the real axis using a large number of points.

The results are discussed in the next chapter.
The dual mean field approach has been implemented in BAND with an LDA exchange-correlation functional (see Appendix B). In this chapter a first comparison will be made between the behaviour of the conventional BAND LDA implementation \[8\] and the DMF approach. It is not intended to provide a full proof of concept, but it does provide motivation for continued research on the method.

This chapter first discusses the specific molecular set-up used for comparison. This is followed by the comparison itself. The chapter is concluded with a prioritized list of recommendations for further research.
Figure 5.1.1: Computer rendered sideview image of an Al-BDA-Al junction. Atomic coordinates are found in Appendix D.

5.1 Set-up

For comparing the DMF and the conventional approach we will use one specific molecular junction: a 1,4-benzene-di-amine molecule between two 3x3 aluminum leads (see Figure 5.1.1).

This is a common junction for studying molecular transport. Usually however, these calculation are performed using gold leads. In gold leads the core electrons experience substantial relativistic effects due to high nucleic charge. So far we have not been able to include in BAND relativistic effects. Aluminum has been used as a light replacement for gold, because of its very similar lattice structure: both gold and aluminum form face centered cubic lattices with lattice constants 406.5 pm and 404.6 pm respectively [23]. There is also an important difference between gold and aluminum. In gold the 6s orbital electron is the binding electron, whereas in Al this is a 3p orbital electron. This difference will become apparent in the next section.

For both the equilibrium and the non-equilibrium DMF densities a single-ζ basis set is used.

---

[1] The high nucleic charge binds the core electrons very strongly. Classically speaking, the relativistic effects can be understood as the very fast orbiting of the electrons as a result of the strong Coulomb force.
For the conventional method a VWN LDA XC functional \(^{24}\) is used. For the DMF method the XC functional as described in Appendix B is utilised. A BAND run script is included in Appendix D that contains specific settings.

5.2 Results

For comparing the DMF and conventional method, we will focus on the HOMO-LUMO gap\(^2\) and investigate the stability of the transmission spectrum with respect to the applied bias voltage.

5.2.1 HOMO-LUMO gap

The HOMO-LUMO gap is an important measure, because LDA is known to underestimate this gap and better methods generally predict larger gaps.\(^3\) This gap is inspected using the transmission spectrum as defined by Eq. 3.15. The conventional LDA transmission spectrum is compared to the non-equilibrium spectrum of the DMF method, as only the non-equilibrium electrons constitute a current. In Figure 5.2.1 both transmissions have been plotted on a semi-logarithmic scale.

For the conventional LDA method, the wide LUMO peak around 0.014 Ha is clearly visible. The HOMO peak is less apparent: this is the narrow peak at approximately -0.084 Ha.\(^4,5\) Combining gives a HOMO-LUMO gap of 0.098 Hartree.

Figure 5.2.1 displays a wide LUMO peak for the DMF method too, that reaches it peak value at 0.051 Ha. At -0.075 Ha a LUMO peak is visible, followed by another, stronger peak at approximately -0.090 Ha. A conservative estimate for the HOMO-LUMO gap is 0.126 Hartree.

The spectra are rather sharply peaked, so the question arises whether the peaks we have located are actually the same HOMO and LUMO states in both methods.\(^6\) To check whether the two HOMO peaks and two LUMO peaks in the two spectra are located right, we will have to find out

\(^{2}\) The gap between the highest occupied and lowest unoccupied state. See Chapter 2 and [25].

\(^{3}\) See Appendix B.

\(^{4}\) The narrowness of this peak is the result of the aluminum. This set-up has been geometrically optimized for gold leads. Coupling of BDA to aluminum is weaker, resulting in less broadening of the peaks.

\(^{5}\) The ‘peak’ just above -0.050 Ha is only 0.1 \(G_0\).

\(^{6}\) For example weak coupling of a LUMO or HOMO state to the leads might result in only a small peak in the spectrum that we may have disregarded.
Figure 5.2.1: Semi-logarithmic plot of the transmission spectra of the conventional LDA method (Green) and the DMF method (Red). In both spectra the Fermi energy is placed at the 0 energy mark. The unit of transmission is the conductance quantum $G_0$. Calculation at a bias of 0.010 a.u. (271 mV).

to what states these peaks correspond. As explained in Chapter 2, without coupling to the leads electrons in the BDA molecule occupy certain molecular orbitals. After coupling these molecular energies are shifted and broadened to form a transmission peak. A system’s transmission peak can therefore be traced back to one specific uncoupled molecular orbital. If in both pictures the peaks result from the same uncoupled molecular orbitals, one knows that the peaks are in fact linked and thus the HOMO-LUMO gap can be compared.

To get a general picture of how this works, an isosurface is plotted of the extended molecular orbital\(^7\) at the found transmission peaks and laid over a computer rendered image of the junction. See Figures 5.2.2b-5.2.2e.

\(^7\)The extended molecular orbital is in fact the real part of the eigenstate of the final Hamiltonian matrix corresponding to the energy of the peak. To calculate this, BAND simply calculates the eigenstate for a selected eigenvalue energy.
Figure 5.2.2: Molecular orbitals at peaks transmission spectrum Figure 5.2.1.
The isosurface represents a fixed absolute amplitude of the molecular orbital, where the blue and red denote the sign of the amplitude. The part that interests us, is the pattern on the benzene ring, because these allow us to link peaks in different spectra. The behaviour in the leads is also important, because this denotes coupling. A state that is isolated on the device, will likely not correspond to a peak in the transmission spectrum.\(^8\)

Clearly visible are the

\[ + - - - \]

\[ + - \text{ and } + + + \]

\[ + - - - \]

patterns\(^9\) visible on the benzene ring, that represent respectively identical HOMO and identical LUMO states. This certifies that the earlier found HOMO and LUMO peaks are indeed linked.

### 5.2.2 Transmission spectrum stability

The bias voltage should have little effect on the transmission spectrum of a set-up.\(^10\) Although the calculations above are performed at a bias voltage of \(0.010\) a.u., similar results are found for other biases. Table 5.2.1 shows the band gap for different biases. Figures 5.2.3a and 5.2.3b indicate that both spectra are only locally affected by bias voltage. The conventional LDA approach does show the HOMO peak to shift slightly downwards with increasing bias, which is not the case for the DMF implementation.

The DMF method predicts a band gap of around \(0.120\) Ha. This is a mean 20% increase compared to the conventional method. A small deviation of the gap size is seen at biases 0.002 and 0.010 Hartree, although the general behaviour is consistent. The conventional LDA is more consistent, at 0.098 ± 0.003. The reason for this difference is not necessarily the method itself, but the width of the transmission peaks: conventional LDA has sharper peaks, allowing more certain determination of the energy level.

---

\(^8\)Although this is not very strict. In the case only one of the leads seems badly bound, an energetically-proximate state that does ‘live’ on the other lead can allow transport to happen. An example is the HOMO state in Fig. 5.2.2b.

\(^9\)Disregarding signs.

\(^10\)The bias voltage should primarily determine the current by specifying the range over which the transmission spectrum should be integrated.
Table 5.2.1: HOMO-LUMO gap at different bias voltages for both methods. Gap is measured from max transmission peak to max transmission peak.

<table>
<thead>
<tr>
<th>Bias (a.u.)</th>
<th>HOMO-LUMO gap (Ha)</th>
<th>Conventional LDA</th>
<th>DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.099</td>
<td>0.112</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>0.101</td>
<td>0.122</td>
<td></td>
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<tr>
<td>0.010</td>
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<td></td>
</tr>
<tr>
<td>0.015</td>
<td>0.098</td>
<td>0.117</td>
<td></td>
</tr>
<tr>
<td>0.020</td>
<td>0.095</td>
<td>0.123</td>
<td></td>
</tr>
</tbody>
</table>

To summarize, the HOMO-LUMO gap in DMF is larger but less stable. The larger size is a good sign, as LDA is known for underestimating this gap and better functionals compensate for this. The minor changes in HOMO-LUMO gap size is the result of the more difficult determination of the gap due to badly coupled states. The location of the HOMO peak seems to be more stable with respect to the conventional LDA method, as it does not show shifting of the peak as a function of bias. No major differences in performance are discovered. Implementations with more set-ups and another XC functional are essential for more insight into this method.

Figure 5.2.3: Transmission spectra for different biases (in a.u.)

5.3 Further research

The results look promising and are a stimulus to further develop this method. A necessary start for improvement will be the inclusion of relativistic effects, for example the ZORA
implementation already present in BAND for the conventional method. This will allow heavier atoms such as gold to be studied. The latter is essential for comparison with literature.

Additionally, more precise exchange-correlation functionals may be implemented. Instead of an LDA approach, a GGA or a more advanced hybrid functional like the CAMY-B3LYP functional can be implemented. Every functional-type is known to have specific deviations,\textsuperscript{11} it will be valuable to explore how a DMF implementation influences these deviations.

Furthermore, there is room for improvement on the precision part. The used single-\(\zeta\) basis set is small, and can be replaced by a larger set of basis functions to increase the solution space and hence increase the accuracy.\textsuperscript{12} This is already possible within the current implementation.

\textsuperscript{11} In the case of LDA this is the overestimation of the HOMO-LUMO gap
\textsuperscript{12} See Appendix C.
In summary, in this thesis an overview is sketched of the dual mean field DFT+NEGF procedure and preliminary results are found using an implementation in the BAND software package.

The conventional DFT method is only valid for ground-state systems, and is hence unable to properly address non-equilibrium set-ups. The dual mean field (DMF) approach to electron transport mathematically solves this problem by using Hershfield [21] non-equilibrium statistics. A non-relativistic LDA DMF approach has been implemented to test performance in practice. Transport calculations in an Al-BDA-Al junction have been analyzed with respect to conventional LDA calculations. The methods are compared on two grounds: the HOMO-LUMO gap and the transmission spectrum stability under changing bias voltages.

The HOMO-LUMO gap of the conventional LDA XC implementation is known to be
underestimated. For biases ranging between 0.002 and 0.020 a.u.,\(^1\) the conventional LDA method yields a HOMO-LUMO gap of 0.098 ± 0.003 Hartree.\(^2\) With the DMF implementation, the HOMO-LUMO gap significantly increases to a mean value of 0.120 Hartree: an increase of 20%. Furthermore, the stability of the transmission spectra is explored as a function of bias. LDA finds all values for the HOMO-LUMO gap size within the range of 0.098 ± 0.003 Hartree. In contrast, the DMF gap size is less consistent, with values ranging from 0.112 to 0.126 Hartree. The increased deviations are however not necessarily the result of the DMF approach, but can be traced back to transmission spectrum: sharper peaks\(^3\) in the conventional LDA method’s spectrum allow more consistent gap size measurement. Inspecting the spectra as a function of bias, the general spectrum behaviour of the conventional and DMF method is observed to be approximately equally stable. At spectrum stability both methods therefore seem to perform equally well, but additional research is required.

The increased HOMO-LUMO gap and unaltered spectrum stability encourage the further development of the method. The results should be regarded as preliminary and more tests are required for definite conclusions. To be able to relate results to standardized tests, the first advancement should be the inclusion of relativistic effects. This allows heavier atoms like gold to be studied. The next step would be the implementation of different XC functionals, like a GGA or hybrid functional. These functionals are more accurate than LDA, although these too are characterized by specific deviations. It is valuable to explore how a DMF approach affects these deviations. At last larger basis sets may be utilized for increased accuracy.

Concisely the dual mean field approach introduces a solid mathematical description of non-equilibrium transport, and provides promising new tools for the future research in nanoscale devices.

\(^1\) 0.001 a.u. ≈ 27.211 mV
\(^2\) 1 Hartree ≈ 27.211 eV
\(^3\) The set-up uses aluminum instead of gold to suppress relativistic effects. The side effect is less coupling between device and leads, which especially in the case of the conventional method expresses itself as a peaked spectrum.
The wave function $\Phi_e$ is a vector in the Hilbert space of many-particle states that describes the behaviour of all electrons in the system. This appendix describes the basis set used to construct $\Phi$. It also illustrates the complexity that arises from working in a $3N$ dimensional space. This method uses the solutions of the unperturbed Hamiltonian $\hat{H}_{se}$ (Eq. 3.3), to find a solution to the total Born-Oppenheimer Hamiltonian (Eq. 3.2).

A.1 Single-electron Hamiltonian

In order to solve the SE using algebraic methods, we need a basis of many-electron states $\Phi_m$ designed to satisfy the non-interacting Hamiltonian.\(^1\) Let us inspect the single-electron Hamiltonian:

$$\hat{H}_{se} = V_{ext}(\mathbf{r}_i) - \frac{1}{2} \nabla_i^2$$

\(^1\)i.e. the many-electron Hamiltonian in which electron-electron effects are absent.
This equation is probably familiar: if $V_{\text{ext}}$ is the Coulomb interaction between nucleus and electron, it describes the Hamiltonian of an electron orbiting a hydrogen-like atom.\(^3\) The solutions to the hydrogen-like Hamiltonian are the exactly known atomic orbitals (AO’s).

In reality, the $V_{\text{ext}}$ term contains the Coulomb attraction by multiple nuclei as well as the bias potential. We can mimic the behaviour of isolated, separated AO’s by taking a linear combination of a finite number of atomic orbitals (LCAO). Using this LCAO the single-electron state $|\varphi_m\rangle$ that satisfies the correct single-electron Hamiltonian can be approximated. Let the individual atomic orbitals be denoted by $|\chi_p\rangle$ and the molecular orbitals by $|\varphi_m\rangle$. The single-electron states can be written in a LCAO manner:

$$
|\varphi_m\rangle = \sum_p c_m^p |\chi_p\rangle ,
$$

(A.1)

with $c_m^p$ a measure for the occupation of the orbital in question.\(^3\)

### A.2 Many-particle non-interacting Hamiltonian

Because of the fermionic nature of electrons, the multiple-particle solution of the non-interacting Hamiltonian for our system of $n$ electrons is an antisymmetrised product of $n$ single-electron wave functions. The result is a so-called Slater determinant, given by Eq. A.2: [12]

$$
\Phi_m(r) = \frac{1}{n!} \begin{vmatrix}
|\varphi_{m_1}(r_1)\rangle & |\varphi_{m_2}(r_2)\rangle & \cdots & |\varphi_{m_n}(r_n)\rangle \\
|\varphi_{m_1}(r_1)\rangle & |\varphi_{m_2}(r_2)\rangle & \cdots & |\varphi_{m_n}(r_n)\rangle \\
\vdots & \vdots & \ddots & \vdots \\
|\varphi_{m_1}(r_1)\rangle & |\varphi_{m_2}(r_2)\rangle & \cdots & |\varphi_{m_n}(r_n)\rangle \\
\end{vmatrix}
$$

(A.2)

with $m$ the vector that denotes of which single-electron wave functions the many-particle wave function $\Phi_m$ is composed. The set of all Slater determinants that can be constructed in this manner forms a complete basis for the $3N$ dimensional Hilbert space.[26]

---

\(^3\)We not necessarily require the charge of the nucleus to be 1, hence hydrogen-like.

\(^3\)If one takes into account spin effects, a spin up $\chi_p^+$ and a spin down $\chi_p^-$ with possibly different occupations $c_m^+$, $c_m^-$ are defined. This research has not included any spin effects and occupations of spin up and down states are always identical.
A.3 Total system’s state $\Phi$

The many particle wave functions $\Phi_m$ each solve the many-particle non-interacting Hamiltonian. The total system’s wave function $\Phi$ is the solution of the electronic Hamiltonian including the electron-electron terms. $\Phi$ is found as a linear combination in the basis set of Slater determinants $\{\Phi_m\}$:

$$\Phi(r) = \sum_m c_m \Phi_m(r).$$  \hspace{1cm} (A.3)

Where $\Phi$ should be normalized such that $\int \Phi(r) \, dr = n$, the total number of electrons in the device.\footnote{Charge neutrality is assumed in the device region. This fixes $N$.}

The complexity of finding $\Phi$ in this manner highlights the astonishing power of density functional theory.
The DFT energy functional includes a term called the exchange-correlation (XC) energy. The exchange energy accounts for the fermionic nature of fermions. Identical particles are prohibited to be at the same position. Consequently, a state with two electrons having the same spin close to each other not increases the state’s energy due to Coulomb interactions, but also as a result for the exchange energy. The anti-symmetric property of the total system’s state is not included in DFT, the exchange energy tries correcting for this.

The correlation energy is basically a measure of how much the electrons influence each other. For example, take a system with two ions and two electrons. If one electron resides on atom $a$, the other electron’s position is due to Coulomb interaction most likely somewhere around atom $b$. DFT does not take this into account, but only looks at the mean location of electron 1: evenly spread between atoms 1 and 2. Consequently, the energy of DFT is too large: it will spread the density of electrons 1 and 2 over atoms $a$ and $b$, raising the Coulomb energy. The correlation term tries to correct this error.
As mentioned in Section 3.2, this research makes use of the Local Density Approximation (LDA) of the exchange-correlation energy.

**B.1 LDA**

An approximation should be used, because for the system at hand an exact functional is unknown. In contrast, very simple systems can be exactly solvable. The functional of a homogeneous electron gas is for example known, and it is exactly this functional LDA uses. LDA assumes the exchange-correlation energy \( E[n](r) \) equals the exchange-correlation energy of a homogeneous electron gas of density \( n(r) \).

This method is inherently unreliable, because it only uses the local density. A critical point at which LDA fails is the Hartree term in the DFT functional. For DFT, the Hartree term results in a self-interaction: an electron's energy is overestimated because it repulses its own charge. The exact exchange-correlation would cancel this, but LDA does not\(^{12}\). As a result the LDA approach leads to an overestimate of the energy.

A more advanced functional is the generalized gradient approximation (GGA), which includes local gradients of the density. Even more advanced functionals use a combination of GGA and a non-DFT approach. LDA delivers a computationally cheap method that is easily implemented, hence this functional has been chosen in this research.

**B.2 Dual Mean Field exchange**

In the dual mean field (DMF) approach (see Chapter 4), the exchange is a bit more complicated as this is where the equilibrium and non-equilibrium densities couple. The correlation energy is assumed to be the same as in the non-DMF case. The LDA exchange energy functional is derived in \([2]\) and is given by:

\[
E_X(n, \eta) = \frac{1}{4} (1 + \eta)^2 \left[ \ln (1 + \eta) + \eta^2 + \eta^4 - 3 \right] \epsilon_{TFD}^{ex}(n),
\]

(B.1)
with

\[
\eta(r) = \frac{n_e(r)}{n_i(r)} \quad \text{(B.2)}
\]

\[
\tilde{\eta}(r) = \left(1 - \frac{\eta}{1 + \eta}\right)^{\frac{1}{3}} \quad \text{(B.3)}
\]

\[
e^{TFD}_{\text{e}}(n_i) = -\frac{1}{4\pi^3}(3\pi^2n_i)^{\frac{1}{3}} \quad \text{(B.4)}
\]

The potentials \(V_{X,e}\) and \(V_{X,n}\) equal \(E_X\) differentiated with respect to respectively \(n_e\) and \(n_n\). This gives

\[
V_{X,e(n)} = \left[\frac{4\epsilon_X}{3(1 + \eta)} + \frac{1}{4}(1 + \eta)^{\frac{2}{3}} \left[4\tilde{\eta}(1 - \tilde{\eta})\ln(1 + \tilde{\eta}) + 4\tilde{\eta}\ln(\tilde{\eta})\right]
+ 4\tilde{\eta}^3 + 4\tilde{\eta}^2\right]\frac{\partial \tilde{\eta}}{\partial \eta} n_e^{TFD}\left(n_i\right) \frac{\partial \eta}{\partial n_e(n)} + E_X(n_i) \frac{\partial E_{TFD}^{X}}{\partial n_e(n)} \quad \text{(B.5)}
\]

with,

\[
\frac{\partial \tilde{\eta}}{\partial \eta} = -\frac{2}{3}(1 - \eta)^{2/3}(1 + \eta)^{2/3} \quad \text{(B.6)}
\]

\[
\frac{\partial \eta}{n_e} = -\frac{\partial n_n}{n_i^2} \quad \text{(B.7)}
\]

\[
\frac{\partial \eta}{n_n} = \frac{\partial n_e}{n_i^2} \quad \text{(B.8)}
\]

\[
\frac{\partial e_{TFD}^{X}}{\partial n_e(n)} = -\frac{1}{3\pi^3}(3\pi^2)^{\frac{1}{3}}n_i^{\frac{1}{3}} \quad \text{(B.9)}
\]
Basis sets electron density

The electron density, a scalar defined in a three-dimensional space, is formed as a linear combination within a basis set of 3D scalars. Any complete basis can give the right result, but for computational purposes one set might be favorable to another. The first computational difference between basis sets is the number of functions within a basis set. Software can only use a finite number of basis functions, so one set might be better at representing the solution than another. The second difference between basis sets is computational difficulty. As calculating the representation of a function within a certain basis ordinarily requires integration, the computing power required to find a representation heavily depends on the integration difficulty of the basis set.

The basis set we use consists of atomic orbitals, centered at each nucleus of the extended molecule. The advantage of using atomic orbitals is that these already satisfy the hydrogen-like Hamiltonian of Eq. 3.3 (see Section A.1). Choosing a set that already satisfies part of the Hamiltonian exactly is physically appealing. In BAND numerical atomic orbitals (NAO’s) are
used, that approximate the exact orbitals.

A last remark should be made on the specific orbitals in the basis set. For valence electrons are responsible for coupling and transport, BAND offers the possibility to use a frozen core approximation: the inner-most orbitals are given a full occupation. This work has used a large frozen core to speed up calculations. BAND offers more options to increase accuracy, including split-valence orbitals \cite{27} and polarization orbitals \cite{28}. These have not been used in the current work. In all cases there is a trade-off between accuracy and computation costs.
BAND calculations are performed using the following run script.

```bash
#!/bin/sh

"$ADFBIN/band" < core

TITLE Leads Tight Binding
BeckeGrid
  Quality Normal
End

ZlmFit
  Quality Normal
End

KSpace
  Quality VeryGood
End

SoftConfinement
  Quality Basic
End

UNITS
  length Angstrom
  angle Degree
END

ATOMS
  Al 1.442497 4.885004 -1.442498
  Al 1.442497 4.885004 1.442498
  Al 0.0 2.845004 0.0
  Al 1.442498 8.965004 -1.442498
  Al 1.442498 8.965004 1.442498
  Al 0.0 6.925004 -2.884996
  Al 0.0 6.925004 2.884996
  Al 0.0 11.005004 0.0
  Al 2.884993 2.845004 0.0
  Al 2.884993 2.845004 -1.442498
  Al 2.884993 2.845004 1.442498
  Al 2.884993 6.925004 -2.884996
  Al 2.884993 6.925004 2.884996
  Al 2.884993 11.005004 0.0
  Al 3.7.112487 4.885004 -1.442498
  Al 3.7.112487 4.885004 1.442498
  Al 3.5.7699 2.845004 0.0
  Al 3.7.112488 8.965004 -1.442498
  Al 3.7.112488 8.965004 1.442498
  Al 3.5.7699 6.925004 -2.884996
  Al 3.5.7699 6.925004 2.884996
  Al 3.5.7699 6.925004 0.0
  Al 3.5.7699 11.005004 0.0
END

Lattice
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End

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  BasisType SZ
  Core Large
  End

XC
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<tr>
<td>Al 8</td>
<td>2.854995</td>
<td>1.952904</td>
</tr>
</tbody>
</table>

END

LiuDFT True
CheckOverlapTol 0.1
LinDFT True
End

mv RUNKF TB.runkf
mv SigmaSCM Sigma.runkf
"SADFBN/ band" << e o r
TITLE Scattering Region
BeckeGrid
Quality Normal
End

UNITs
length Ångström
angle Degree

END

ATOMs
Al 1 1.444947 4.885004 1.444948
Al 2 1.444947 4.885004 1.444948
Al 3 1.444947 4.885004 1.444948
Al 4 1.444947 4.885004 1.444948
Al 5 1.444947 4.885004 1.444948
Al 6 1.444947 4.885004 1.444948
Al 7 1.444947 4.885004 1.444948
Al 8 1.444947 4.885004 1.444948

END

LiuDFT True
CheckOverlapTol 0.1
LinDFT True
End

mv RUNKF align.runkf
"SADFBN/ band" << e o r
TITLE Scattering Region
BeckeGrid
Quality Normal
End

UNITs
length Ångström
angle Degree

END

ATOMs
Al 1 1.444947 4.885004 1.444948
Al 2 1.444947 4.885004 1.444948
Al 3 1.444947 4.885004 1.444948
Al 4 1.444947 4.885004 1.444948
Al 5 1.444947 4.885004 1.444948
Al 6 1.444947 4.885004 1.444948
Al 7 1.444947 4.885004 1.444948
Al 8 1.444947 4.885004 1.444948

END


[3] SCM. *BAND2017*. Theoretical Chemistry, Vrije Universiteit Amsterdam. A modified version of this code has been used.


