

Foundation for a parallel time-dependent
density functional theory simulator in a
spherical harmonic basis using the exact
exchange energy functional

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Abstract

An intuitive introduction to density functional theory using the Kohn-Sham method is presented and extended to the time-domain. Further an overview of different types of exchange-correlation functionals is given, with particular focus on the optimised effective potential and the KLI-approximation.

Parallel numerical incorporation of this theory in a spherical harmonic basis is discussed and calculated.

Finally proof of concept simulations of helium and beryllium is shown. From these preliminary results it is concluded that the method is not only numerically fast, but also comparable accurate, to the much more numerically demanding Hartree-Fock method.

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Preface

This master thesis presents the work I have done on my master studies in the period Dec. 2010 - Dec. 2011. The end goal of this project, is to create a parallel program capable of simulating time dynamics of atoms and molecules hit by intense laser pulses using time-dependent density functional theory. The background for this project is that the group is already in possession of a very fast, versatile and parallel single-active electron time-dependent Schrödinger equation solver. The initial idea was that I should be able to write an enveloping master program, which could use the previous program without much need for editing.

Right from the start the work has been two-sided. On one side I had the numerical aspect, here I had to first learn Fortran/MPI. On the other side I had to learn density functional theory and its time-dependent counterpart, both of which I had no prior knowledge.

Both areas started out great, I learned the basic theories, the programming language and wrote a parallel and independent master program.

That was when the trouble started.

On the numerical side it started when I tried to integrate the new and the old program. It quickly became apparent that there was no way these two independent programs could be simply connected. Instead I would have to code my program directly into the old one, which would require intimate knowledge of how the old program with more than 5000 lines of code worked.

Regarding the underlying physics it slowly became apparent that the exchange-correlation potential we had initially envisioned for the project would not be feasible to use. Instead we decided to go with a more accurate and much more complicated exchange-correlation potential, the optimised effective potential with the KLI-approximation.

In august/september I attended an almost month long conference in Stockholm with the topic: "Quantum Dynamics in the Time Domain". Here I discussed density functional theory with a few international experts. This was very illuminating for my understanding of density functional theory, but it also helped me get a much broader perspective on the whole area of physics, which density functional theory falls within.

So this was the background I had, when I started writing this thesis.

Notation

Atomic units (a.u.) is used throughout this thesis, unless otherwise indicated. In atomic units the Bohr radius, a_0 , the elementary charge, e , the electronic mass, m_e , and the reduced Planck constant, \hbar , are all set to unity.

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Abbreviation

CG	Clebsch-Gordan
DFT	Density functional theory
GEA	Gradient expansion approximation
GGA	Generalized gradient approximation
HEG	Homogeneous electron gas
HF	Hartree-Fock
HK	Hohenberg-Kohn
ITP	Imaginary time propagation
KLI	Krieger, Li, & Iafrate
KS	Kohn-Sham
LDA	Local density approximation
LSDA	Local spin density approximation
meta-GGA	meta- Generalized gradient approximation
OEP	Optimised effective potential
RG	Runge-Gross
SAE-TDSE	Single active electron time-dependent Schrödinger equation
TDDFT	Time-dependent density functional theory
TDSE	Time-dependent Schrödinger equation
TF	Thomas-Fermi
xc	exchange-correlation

Chapter 0

Introduction

The purpose of this master thesis is to contain the relevant physical knowledge needed in order to create a parallel program capable of simulating time dynamics of atoms and molecules hit by intense laser pulses using time-dependent density functional theory. Density functional theory shifts the attention from the wavefunction to the, computationally much simpler, density. This makes density functional theory much cheaper to solve numerically than the Schrödinger equation. If one could find a general exact exchange-correlation functional, density functional theory could solve any system exact. One problem when using density functional theory, is that some interesting phenomena become troublesome to calculate. For instance the way to calculate ionisation using the density is currently an open question. Other phenomena are made no more difficult to find by using density functional theory. An example of this could be high-order harmonic generation, which relies strictly upon the density, and is key in making attosecond science.

The assumption in this thesis is that people are familiar with quantum mechanics but not necessarily density functional theory.

Chapters one & two contain a general introduction into density functional theory. Density functional theory can be approached in a lot of ways, the route I have chosen, is the one which I believe to be the most intuitive.

Chapter three is dedicated to the creation of a single potential called the optimised effective potential. The reason why we spend a whole chapter on this potential is because it is the one which will be used in our program.

Chapter four makes the crossing into the time-domain. Once again the purpose is to give an intuitive introduction which connects the first three chapters to this one. The time-dependent density functional theory which enables this crossover eluded us for almost a year before we finally solved it correctly. The problem was that during the theory

a certain commutator needs to be calculated, which no one seems to show. A calculation of this elusive commutator is shown in appendix E.

Chapter five gives greater detail about how our numerical implementation is being done. It also illuminates different parallelisation schemes which could be used in the creation of a simulator.

Chapter six converts the whole theory into reduced spherical harmonics. This is done because our program uses a spherical harmonic basis.

Chapter seven shows the few preliminary results our program is thus far able to produce.

Chapter eight rounds this thesis off with a conclusion and a future perspective.

Chapter 1

Time-independent quantum systems

Quantum mechanics can be formulated in several ways. But the most used formalism is the Schrödinger picture, in which the fundamental equations all quantum mechanical systems must obey are known as the Schrödinger equations.

In the simple case of time-independent systems, the Schrödinger equation is given as:

$$\hat{H}\Psi = E\Psi, \quad (1.1)$$

where E is the energy, \hat{H} is the Hamiltonian and Ψ is the wavefunction. In general the Hamiltonian consists of two terms:

$$\hat{H} = \sum_{i=1}^N \hat{H}^{(1)}(i) + \frac{1}{2} \sum_{i,j=1}^N \hat{H}^{(2)}(i,j), \quad (1.2)$$

the first term $\hat{H}^{(1)}(i)$ is a single-particle interaction, whereas the second term $\hat{H}^{(2)}(i,j)$ is a two-particle interaction - the $1/2$ is included to counter the double counting.

The usual job within time-independent quantum systems is: Given a certain Hamiltonian, find the corresponding wavefunction¹. Finding the wavefunction of a system is relatively easy for some systems, while downright impossible for others.

Introductions to quantum mechanics usually analyse systems like the free particle, the harmonic oscillator and the infinite square well, all of which can be done analytically. A common trend among these systems is that their Hamiltonians consist purely of single-particle interaction, and upon closer analysis it turns out that quantum mechanical systems with purely single-particle interaction are in

¹Remember a system's wavefunction contains all the knowledge we could possibly need about a system.

general cheap to solve numerically. If for instance we consider a box in Cartesian coordinates with n grid points along each coordinate, the total box consists of $N_{box} = n^3$ grid points. Now each of the N particles need to be described in this box, this gives a total of $N_{system} = N \cdot n^3$ points which need to be calculated. We see that such a system scales linearly with the number of particles in the box. Hence this is doable even for relatively large systems.

On the other hand quantum mechanical systems with two-particle interactions are in general expensive to solve numerically, in fact for all but the very simplest systems it is not doable even with modern computers. We see this by again considering our box which consists of $N_{box} = n^3$ grid points. Now each of the N particles need to be described in this box, but each particle depend upon all the other $N - 1$ particles in each point, hence we get: $N_{system} = N \cdot (n^3)^N$. So for interacting particle systems the complexity scales exponentially with the number of particles in the box. Hence for a reasonable sized box this is barely doable for two-particle systems. In general we call systems which contain two-particle interactions for many-body quantum systems.

Unfortunately most realistic systems contain two-particle interaction, among these are both atoms and molecules, which we hope to describe. Hence in this thesis we focus on the subset of quantum mechanical systems which falls into the category of many-body quantum systems.

1.1 Many-body quantum systems

The essence of many-body quantum systems is the two-particle interaction, an interaction which cannot be solved analytically and in general is too numerically demanding to calculate. Because of this the usual approach is to use approximations to move any further.

In general there are two kinds of approximations one can make. Either you turn the quantum mechanical system of interacting particles into a quantum mechanical system of non-interacting particles, or you turn the system into a semi-classical system of interacting particles.

Realistic quantum systems often contain a combination of electrons and nuclei. Because of the huge mass difference between these two types of particles one almost always employ the Born-Oppenheimer approximation, where we separate the motion of the nuclei and the electrons. With the Born-Oppenheimer approximation

we get a Schrödinger equation of the form:

$$\begin{aligned}\hat{H}\Psi &= [\hat{T}_e + \hat{V}_{en} + \hat{V}_{ee}] \Psi \\ &= \left[\sum_i^N \frac{-\nabla_i^2}{2} + \sum_i^N V_{en}(\mathbf{r}_i) + \sum_{i<j}^N V_{ee}(\mathbf{r}_i, \mathbf{r}_j) \right] \Psi = E\Psi,\end{aligned}\quad (1.3)$$

where the first term in the bracket is the electrons kinetic energy, the second the electron-nuclei potential, the third the electron-electron repulsion and Ψ is the electronic many-body wavefunction dependent on all the electrons, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$.

Even though we have used the Born-Oppenheimer approximation the above equation still contains two-particle interaction in the form of the electron-electron potential, hence we need to do more before simulations can be made.

For weakly interacting systems a perturbative approach might be the best solution. But if we want good results in general we need another method.

One method is to employ the Hartree-Fock (HF) approximation, which separates the quantum mechanical many-body problem into N single particle problems while retaining Pauli's exclusion principle. More precisely it is assumed that the many-body wavefunction can be approximated by a single Slater determinant¹. The HF approximation is a self-consistent theory and is usually very precise, although it reduced the degrees of freedom dramatically. In fact even with HF approximation many systems are still too complicated to calculate, which is why we look for an alternative route.

In our case the alternative route is called density functional theory (DFT).

1.2 Density functional theory

The idea behind DFT, is to show that the ground state observables of a many-particle quantum system can be described exactly by the total density². It should however be noted already now, that although the theory in itself is exact, approximations will still enter in actual calculation due to our inability to find an exact functional which describes any system.

The first actual formulation of a density functional theory was derived by Hohenberg and Kohn in 1964[1].

¹It is only a determinant if we consider fermions, in the case of bosons the approximation gives what is known as a permanent.

²The density is a variable of only three degrees of freedom hence if we can accurately describe a system by its density alone we have reduced the amount of computation dramatically!

1.2.1 Hohenberg-Kohn's theory of DFT.

Hohenberg & Kohn's famous article actually contains several theorems, but the first and by far most important is the existence theorem.

The first theorem states that the ground state properties of any many-electron system is uniquely determined by the electron density, up to an additive constant.

The proof given in the following is not the original proof by Hohenberg and Kohn, but the general method and idea is the same.

The foundation which DFT is built on is:

The Schrödinger equation, written as:

$$(\hat{T} + \hat{V} + \hat{W}) \Psi = E\Psi, \quad (1.4)$$

where \hat{T} is the kinetic energy, \hat{V} is the external energy, and \hat{W} is the interaction energy. If we assume that Ψ is the ground state wavefunction, then \hat{T} and \hat{W} are fixed. This means that the wavefunction, Ψ , is a functional of the external potential: $\Psi[v]$. The solution to the Schrödinger equation is then:

$$(\hat{T} + \hat{V} + \hat{W}) \Psi[v] = E\Psi[v]. \quad (1.5)$$

The job is now to prove that the external potential, v , is determined by the ground state density¹, $\rho(\mathbf{r})$.

Theorem 1.1. (Hohenberg-Kohns Theorem) *Assume a non-degenerate ground state², and define a general external potential:*

$$\hat{V} = \sum_i v(\mathbf{r}_i). \quad (1.6)$$

The external potential, v , can then be determined uniquely up to an arbitrary constant by the ground state density, $\rho(\mathbf{r})$.

So just to illuminate the problem completely, we define the mapping $\check{C} : \tilde{v} \rightarrow \tilde{\Psi}$, which goes from the set of external potential \tilde{v} to the set of ground state wavefunctions $\tilde{\Psi}$. Similarly we define the mapping $\check{D} : \tilde{\Psi} \rightarrow \tilde{\rho}$, which goes from the set of ground state wavefunctions, $\tilde{\Psi}$, to the set of v -representable³ ground state densities, $\tilde{\rho}$.

¹Actually v is only determined up an arbitrary constant, but since such a constant has no physical meaning it should be of no concern.

²The degenerate case will be handled in section 1.2.2, though it should not cause too much concern since any degenerate system can be made non-degenerate by adding an infinitesimal perturbation.

³A density is called v -representable, if there exists some external potential, such that the density can be created from an antisymmetric ground state wavefunction with the external potential. This will be further explored in section 1.2.2.

From 1.5 we see that map \check{C} exists. The fact that map \check{D} exists is trivial since we know that $\rho = |\Psi|^2$. By combining the two maps we get a mapping from the external potentials to the densities.

What we seek in DFT is the inverse mapping, we get this by proving that both map \check{C} and \check{D} are invertible.

Proof. (Step 1 : Proof that \check{C} is invertible, i.e. that there is a 1-1 correspondence between external potential and ground state wavefunctions.)
proof by *reductio ad absurdum*.

Assume \check{C} is not invertible. That means there exists two potentials which differ by more than a constant, $v_1 \neq v_2 + C$, and yields the same wavefunction, Ψ , up to a trivial phase-factor $\Psi_1 = e^{i\alpha}\Psi_2, \alpha \in \mathbb{R}$, which we ignore. Hence we get:

$$\hat{H}_1\Psi = (\hat{T} + \hat{V}_1 + \hat{W})\Psi = E_1\Psi \quad (1.7)$$

$$\hat{H}_2\Psi = (\hat{T} + \hat{V}_2 + \hat{W})\Psi = E_2\Psi \quad (1.8)$$

By subtracting the two equations we get:

$$(\hat{V}_1 - \hat{V}_2)\Psi = (E_1 - E_2)\Psi \quad (1.9)$$

If the Lebesgue measure of Ψ is different from zero¹, we can divide it out, and thus we get:

$$\hat{V}_1 - \hat{V}_2 = E_1 - E_2 = C. \quad (1.10)$$

So our two potentials differ by no more than a constant, in contradiction to our initial assumption. Hence \check{C} is invertible. \square

Proof. (Step 2 : Proof that \check{D} is invertible, i.e. that there is a 1-1 correspondence between non degenerate ground state wavefunctions and ground state densities.)

proof by *reductio ad absurdum*.

Assume \check{D} is not invertible, then there exists two different wavefunctions, Ψ_1 & Ψ_2 , which give the same density, ρ .

The energy corresponding to Ψ_1 is given as:

$$\begin{aligned} E_1 &= \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle \\ &= \langle \Psi_1 | \hat{H}_2 + \hat{V}_1 - \hat{V}_2 | \Psi_1 \rangle \\ &= \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle + \langle \Psi_1 | \hat{V}_1 - \hat{V}_2 | \Psi_1 \rangle, \end{aligned} \quad (1.11)$$

by switching the second term from Dirac notation to normal notation we get:

$$E_1 = \langle \Psi_1 | \hat{H}_2 | \Psi_1 \rangle + \int d\mathbf{r} \rho(\mathbf{r}) [v_1(\mathbf{r}) - v_2(\mathbf{r})]. \quad (1.12)$$

¹Which it will be whenever the potential is finite, as it is in any real systems.

Now we use the variational principle and the fact that $\Psi_1 \neq \Psi_2$:

$$E_1 > E_2 + \int d\mathbf{r} \rho(\mathbf{r}) (v_1(\mathbf{r}) - v_2(\mathbf{r})). \quad (1.13)$$

By interchanging indices 1 and 2 and repeating the calculation done in (1.11-1.13) we get:

$$E_2 > E_1 + \int d\mathbf{r} \rho(\mathbf{r}) (v_2(\mathbf{r}) - v_1(\mathbf{r})). \quad (1.14)$$

By adding (1.13) and (1.14) we obtain:

$$E_1 + E_2 > E_2 + E_1, \quad (1.15)$$

which is clearly a contradiction, and hence \check{D} is invertible. \square

We have shown that map \check{C} and map \check{D} is invertible, hence the combined map $\check{C} \circ \check{D}$ is also invertible. This means that there exists a 1-1 correspondence between external potentials and densities.

Existence of a density variational principle

In the previous it was shown that the potential, $v(\mathbf{r})$, is a functional of the ground state density, $\rho(\mathbf{r})$. Through the Schrödinger equation we then know that the wavefunction, Ψ , is also a functional of the density. Because of this, any ground state observable, O , is a functional of the density:

$$O[\rho] = \langle \Psi[\rho] | \hat{O} | \Psi[\rho] \rangle. \quad (1.16)$$

Since the ground state energy is a ground state observable we have:

$$\begin{aligned} E[\rho] &= \langle \Psi[\rho] | \hat{T} + \hat{V}[\rho] + \hat{W} | \Psi[\rho] \rangle \\ &= \langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \rangle + \langle \Psi[\rho] | \hat{V}[\rho] | \Psi[\rho] \rangle \\ &= \langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \rangle + \int d\mathbf{r} \rho(\mathbf{r}) v[\rho](\mathbf{r}). \end{aligned} \quad (1.17)$$

The first term can be split and written as a kinetic energy functional, $T[\rho]$, and a two-particle interaction energy functional, $W[\rho]$:

$$\begin{aligned} E[\rho] &= \langle \Psi[\rho] | \hat{T} | \Psi[\rho] \rangle + \langle \Psi[\rho] | \hat{W} | \Psi[\rho] \rangle + \int d\mathbf{r} \rho(\mathbf{r}) v[\rho](\mathbf{r}) \\ &= T[\rho] + W[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v[\rho](\mathbf{r}). \end{aligned} \quad (1.18)$$

It is usual practice to gather $T[\rho]$ and $W[\rho]$ into one functional called the Hohenberg-Kohn energy functional $F_{HK}[\rho]$:

$$F_{HK}[\rho] = T[\rho] + W[\rho], \quad (1.19)$$

when inserted we get:

$$E[\rho] = F_{HK}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v[\rho](\mathbf{r}). \quad (1.20)$$

Note that $F_{HK}[\rho]$ is an internal functional independent of the external potential and only dependent on the internal interaction, hence for all systems with coulombic interparticle interaction it is the same¹.

If we fix the external potential as, v_0 , we only vary over the density and hence we get the density variational principle:

$$E_{v_0}[\rho] = \langle \Psi[\rho] | \hat{T} + \hat{V}_0 + \hat{W} | \Psi[\rho] \rangle > E_0, \quad \rho \neq \rho_0, \quad (1.21)$$

where E_0 is the ground state energy and ρ_0 is the ground state density.

The ground state density can be obtained by minimizing the energy functional, $E_{v_0}[\rho]$, with regard to the density. This can be written as:

$$\frac{\delta E_{v_0}[\rho]}{\delta \rho(\mathbf{r})} = 0, \quad (1.22)$$

which due to (1.20) is equivalent to:

$$\frac{\delta F_{HK}[\rho]}{\delta \rho(\mathbf{r})} = -v_0(\mathbf{r}). \quad (1.23)$$

So in the end, solving DFT boils down to solving (1.23). The right hand side is nothing but the external potential, which is assumed known. The left hand side is the determining equation, which gives us the density. Determining an explicit expression for the left side is all that we now need.

But before we move on with the functional F_{HK} , the next section will be about DFT's domain of validity, and how we can extend the domain assumed in Hohenberg-Kohn's theory.

1.2.2 Beyond Hohenberg-Kohn's domain

In the previous section a proof of DFT was given. But for the sake of clarity, we skipped lightly over the domain in which the theory is applicable. We now seek to rectify this.

During the DFT proof it was mentioned that the density has to be v -representable.

A density is said to be v -representable, if there exist some external potential, which through the Schrödinger equation can create an antisymmetric ground state wavefunction, that in turn can create the desired density.

¹Hohenberg-Kohn and several others use the term universal functional for such an independent functional.

The question is now how big is the domain of v -representable densities?

Hohenberg and Kohn wrote in their original paper that they believed that all densities except some pathological distributions are v -representable, a point which they were unable to prove. The problem is that no one else has thus far been able to prove exactly how big the domain of v -representable densities is, thus apart from the definition we do not know which conditions makes a density v -representable. Many examples have been given through the decades of "reasonable" densities which have been shown to not be v -representable [2], even some single particle states have been shown to be outside the v -representable domain [3].

This is a serious problem since our universal and defining functional $F_{HK}[\rho]$ given in (1.23) is only defined for v -representable densities.

Luckily, it turns out that it is not strictly necessary to limit the densities to the v -representable domain in order to prove DFT. Levy showed [4] that the theory of DFT can be extended to the domain of N -representability.

Levy defined a N -representable function as a function which can be obtained from some antisymmetric wavefunction, mathematically Gilbert showed that this can be written as[5]:

A density $\rho(\mathbf{r})$ is said to be N -representable if:

$$\rho(\mathbf{r}) \geq 0 \quad , \quad \int \rho(\mathbf{r}) d\mathbf{r} = N \quad , \quad \int |\nabla \rho(\mathbf{r})|^{1/2}|^2 d\mathbf{r} < \infty. \quad (1.24)$$

The set of v -representable densities is clearly contained in the larger set of N -representable densities.

In order to prove DFT on the larger N -representable density domain, a constrained search is used as proposed by Levy[4].

Proving DFT with N -representable densities using constrained search.

Let $\rho_0(\mathbf{r})$ be the ground state electron density. Let Ψ_0 be the ground state wavefunction.

We now show how Ψ_0 can be constructed from $\rho_0(\mathbf{r})$. This is not trivial since each $\rho_0(\mathbf{r})$ correspond to an infinite number of antisymmetric wavefunctions Ψ_{ρ_0} , and in this infinite set we have to connect $\rho_0(\mathbf{r})$ to the true ground state, Ψ_0 .

From the variational principle we know that the true ground state has the lowest energy:

$$\langle \Psi_{\rho_0} | \hat{H} | \Psi_{\rho_0} \rangle \geq \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E_0, \quad (1.25)$$

where \hat{H} is the usual Hamiltonian for the N-electron system. By separating the external potential from the kinetic and interaction terms, we get:

$$\begin{aligned} \langle \Psi_{\rho_0} | \hat{T} + \hat{W} | \Psi_{\rho_0} \rangle + \int v(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r} \geq \langle \Psi_0 | \hat{T} + \hat{W} | \Psi_0 \rangle \\ + \int v(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}. \end{aligned} \quad (1.26)$$

Now because the external potential is only a functional of the density and not the wavefunction, it is the same on both sides and can be subtracted:

$$\langle \Psi_{\rho_0} | \hat{T} + \hat{W} | \Psi_{\rho_0} \rangle \geq \langle \Psi_0 | \hat{T} + \hat{W} | \Psi_0 \rangle. \quad (1.27)$$

Hence for a fixed density, ρ_0 , the ground state, Ψ_0 , minimizes the kinetic and interaction term, which is precisely the universal functional $F_{HK}[\rho_0]$ defined by Hohenberg-Kohn for any v -representable density. In other words:

$$F_{HK}[\rho_0] = \langle \Psi_0 | \hat{T} + \hat{W} | \Psi_0 \rangle = \min_{\Psi \rightarrow \rho_0} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle. \quad (1.28)$$

So in the above we search through all wavefunctions which gives us the density ρ_0 . This is what is meant by a constrained search.

Instead of using the Hohenberg-Kohn functional, we instead define a new functional $F[\rho]$ as:

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle, \quad (1.29)$$

which is not only defined on the larger N -representable domain, but can also handle degeneracy without problems¹. We see that the functionals are consistent:

$$F_{HK}[\rho_0] = F[\rho_0], \quad (1.30)$$

if ρ_0 is v -representable.

This new functional can not only be used to prove DFT, but also extend the domain of the density variational principle. This is easily seen by writing the variational principle:

$$E_0 = \min_{\Psi} \langle \Psi | \hat{T} + \hat{W} + \hat{V} | \Psi \rangle, \quad (1.31)$$

and splitting the minimization in two steps:

$$E_0 = \min_{\rho} \left\{ \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} + \hat{V} | \Psi \rangle \right\}, \quad (1.32)$$

¹Greater mathematical details can be found in [6].

where the inner minimization is the constrained search over all wavefunctions Ψ giving a specific density ρ , while the outer minimizes over all densities.

By separating the external potential, we get:

$$E_0 = \min_{\rho} \left\{ \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \right\}, \quad (1.33)$$

note that the external potential term does not contain any wavefunction dependence, hence the inner minimization is only relevant for the first term, which is nothing but the functional we recently defined as $F[\rho]$:

$$E_0 = \min_{\rho} \left\{ F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \right\}, \quad (1.34)$$

In section 1.2.1 we defined the v -representable energy functional $E[\rho]$. We now naturally expand this to the N -representable domain as:

$$E[\rho] = F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}. \quad (1.35)$$

So just as expected we get the ground state by minimizing the energy-functional:

$$E_0 = \min_{\rho} E[\rho]. \quad (1.36)$$

We have extended DFT and the density variational principle to the N -representable domain.

What is left now is to determine $F[\rho]$.

1.3 The Kohn-Sham method

Many approximations have been tried and tested to find the universal functional $F[\rho]$. Already back in 1927 Thomas-Fermi (TF) were making approximations in order to determine the functional [7, 8]. TF made a model, where the idea was to approximate the kinetic energy. TF's crude model gave surprisingly good results for many systems, but fails for molecular systems [9, p. 50].

A better way to tackle the system is to use the general Kohn-Sham (KS) approach. Instead of considering the complicated many-body system, a fictitious system of non-interacting particles is created. The system is created in such a way that the density of the fictitious system and the real system are identical. Through the use of the 1-1 correspondence between density and external potential, as given in DFT, we can ensure that any density encountered in a real system

can be reproduced by a fictitious system, using an effective external potential¹.

To get started we use the fact that the 1-1 correspondence derived in DFT was valid for any kind of two-particle interaction. In particular it is certainly valid for the case of a non-interacting system.

Let \hat{H}_s be a single particle Hamiltonian:

$$\hat{H}_s[\rho] = \hat{T}_s + \hat{V}_s[\rho]. \quad (1.37)$$

Let $\Phi_s[\rho]$ be the corresponding ground state KS wavefunction which satisfies:

$$\hat{H}_s[\rho]\Phi_s[\rho] = E_s\Phi_s[\rho], \quad (1.38)$$

where the density, ρ , is given from the density operator, $\hat{\rho}$, as:

$$\rho(\mathbf{r}) = \langle \Phi_s[\rho] | \hat{\rho} | \Phi_s[\rho] \rangle. \quad (1.39)$$

The ground state KS wavefunction can be written as a slater determinant of the KS orbitals $\varphi_{i\sigma}(\mathbf{r}_i)$:

$$\Phi_{s\sigma}[\rho](\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{bmatrix} \varphi_{1\sigma}(\mathbf{r}_1) & \cdots & \varphi_{1\sigma}(\mathbf{r}_N) \\ \vdots & \ddots & \vdots \\ \varphi_{N\sigma}(\mathbf{r}_1) & \cdots & \varphi_{N\sigma}(\mathbf{r}_N) \end{bmatrix}. \quad (1.40)$$

Because the KS equations are decoupled an often more illuminating way to write the KS equations are through the single particle orbitals. When written in orbital form, the KS equation is given as:

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_s(\mathbf{r}, t) \right] \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_i \varphi_{i\sigma}(\mathbf{r}), \quad i = \{1, \dots, N_\sigma\} \quad (1.41)$$

$$\rho(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N_\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2. \quad (1.42)$$

The above is the starting point in the KS model, and the goal is still to find an expression for the universal functional F_{HK} .

We start our search by looking at the total energy functional, which F_{HK} is closely connected with. The total energy of the system can be found by summing all the decoupled term's eigenenergies:

$$E_s[\rho] = \sum_{\sigma} \sum_{i=1}^{N_\sigma} \varepsilon_i[\rho]. \quad (1.43)$$

¹By using this approach we once again limit our domain to v -representable densities. A less clear but more general method of introducing Kohn-Sham which preserves N -representability, can be found in [9].

This total energy can also be written as:

$$E_s[\rho] = \langle \Phi_s[\rho] | \hat{T}_s + \hat{V}_s | \Phi_s[\rho] \rangle, \quad (1.44)$$

note that there is no interparticle interaction term due to the fact that we are in the non-interacting KS model.

By splitting the two terms and using the fact that $\hat{V}_s = \int d\mathbf{r} v_s(\mathbf{r}) \hat{\rho}(\mathbf{r})$, we get:

$$E_s[\rho] = \langle \Phi_s[\rho] | \hat{T}_s | \Phi_s[\rho] \rangle + \langle \Phi_s[\rho] | \int d\mathbf{r} v_s(\mathbf{r}) \hat{\rho}(\mathbf{r}) | \Phi_s[\rho] \rangle. \quad (1.45)$$

The kinetic term is contracted, while in the second term all but the density operator is moved outside the bracket. This is then nothing more than the density as given in (1.39), hence we get:

$$E_s[\rho] = T_s[\rho] + \int d\mathbf{r} v_s(\mathbf{r}) \rho(\mathbf{r}), \quad (1.46)$$

where we introduced the kinetic single-particle energy functional $T_s[\rho]$:

$$T_s[\rho] = \langle \Phi_s[\rho] | \hat{T}_s | \Phi_s[\rho] \rangle. \quad (1.47)$$

$T_s[\rho]$ is well defined, and easy to calculate. The idea is that $T_s[\rho]$ will contain the essence of the actual kinetic energy, $T[\rho]$, of the many-body system. The difference between the two kinetic energies is part of what we define as the exchange-correlation energy:

$$E_{xc}[\rho] = F[\rho] - E_H[\rho] - T_s[\rho], \quad (1.48)$$

where $E_H[\rho]$ is the direct-energy also known as the Hartree energy [10, p. 386], which is given as:

$$E_H[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (1.49)$$

From this we finally get an expression for the universal functional $F[\rho]$:

$$F[\rho] = E_{xc}[\rho] + E_H[\rho] + T_s[\rho]. \quad (1.50)$$

This expression for the HK functional can be inserted into the defining equation which was given in (1.23), we then get:

$$v_{xc}[\rho](\mathbf{r}) + v_H[\rho](\mathbf{r}) + \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = -v_0(\mathbf{r}), \quad (1.51)$$

where $v_H[\rho]$ is the Hartree potential, and $v_{xc}[\rho]$ is the exchange-correlation potential defined by the equations:

$$v_H[\rho](\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (1.52)$$

$$v_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \quad (1.53)$$

In order to progress further with (1.51), $\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}$ is calculated:

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = \frac{\delta}{\delta \rho(\mathbf{r})} \langle \Phi_s[\rho] | \hat{T}_s | \Phi_s[\rho] \rangle. \quad (1.54)$$

The single particle kinetic operator is independent of the density hence we get:

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = \langle \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} | \hat{T}_s | \Phi_s[\rho] \rangle + \langle \Phi_s[\rho] | \hat{T}_s | \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} \rangle. \quad (1.55)$$

The kinetic term is related to the Hamiltonian through (1.37), when inserted we get:

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = \langle \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} | \hat{H}_s - \hat{V}_s | \Phi_s[\rho] \rangle + \langle \Phi_s[\rho] | \hat{H}_s - \hat{V}_s | \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} \rangle, \quad (1.56)$$

which we split to get:

$$\begin{aligned} \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = & \left[\langle \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} | \hat{H}_s | \Phi_s[\rho] \rangle + \langle \Phi_s[\rho] | \hat{H}_s | \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} \rangle \right] \\ & - \left[\langle \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} | \hat{V}_s | \Phi_s[\rho] \rangle + \langle \Phi_s[\rho] | \hat{V}_s | \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} \rangle \right]. \end{aligned} \quad (1.57)$$

On the first part we use the fact that Φ_s are eigenstates to the Hamiltonian \hat{H}_s with eigenvalue E_s . In the second part we use that $\hat{V}_s = \int d\mathbf{r}' v_s(\mathbf{r}') \hat{\rho}(\mathbf{r}')$:

$$\begin{aligned} \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = & E_s \left[\langle \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} | \Phi_s[\rho] \rangle + \langle \Phi_s[\rho] | \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} \rangle \right] - \int d\mathbf{r}' v_s(\mathbf{r}') \\ & \left[\langle \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} | \hat{\rho}(\mathbf{r}') | \Phi_s[\rho] \rangle + \langle \Phi_s[\rho] | \hat{\rho}(\mathbf{r}') | \frac{\delta \Phi_s[\rho]}{\delta \rho(\mathbf{r})} \rangle \right]. \end{aligned} \quad (1.58)$$

By pulling the derivative out in front we contract the terms:

$$\begin{aligned} \frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = & E_s \frac{\delta}{\delta \rho(\mathbf{r})} \langle \Phi_s[\rho] | \Phi_s[\rho] \rangle \\ & - \int d\mathbf{r}' v_s(\mathbf{r}') \frac{\delta}{\delta \rho(\mathbf{r})} \langle \Phi_s[\rho] | \hat{\rho}(\mathbf{r}') | \Phi_s[\rho] \rangle. \end{aligned} \quad (1.59)$$

The first part is zero since it contains the derivative of a constant number. In the second part we use the definition of the density as

given in (1.39), hence we get:

$$\begin{aligned}\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} &= - \int d\mathbf{r}' v_s(\mathbf{r}') \frac{\delta}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}') \\ &= - \int d\mathbf{r}' v_s(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}').\end{aligned}\quad (1.60)$$

So in the end we find:

$$\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})} = -v_s(\mathbf{r}). \quad (1.61)$$

By inserting (1.61) into (1.51) we then get:

$$v_s[\rho](\mathbf{r}) = v_{xc}[\rho](\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_0(\mathbf{r}). \quad (1.62)$$

So once we find $v_{xc}[\rho](\mathbf{r})$ we can use the above as a defining equation for the KS-potential $v_s[\rho](\mathbf{r})$. By combining this with the KS equation we finally have an explicit expression for the density.

So just to recap, the defining system of equations which we thus far have found, by the use of DFT and KS is:

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_i \varphi_{i\sigma}(\mathbf{r}) \quad (1.63)$$

$$\rho(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\varphi_{i\sigma}(\mathbf{r})|^2 \quad (1.64)$$

$$v_s[\rho](\mathbf{r}) = v_{xc}[\rho](\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_0(\mathbf{r}) \quad (1.65)$$

$$v_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \quad (1.66)$$

So once an approximation to $E_{xc}[\rho]$ is found the only unknown will be the density. The density will then be found by solving the system self-consistently¹. The quest for a good approximation to the exchange-correlation energy functional begins in the following chapter.

¹By self-consistently we mean: Given some random trial orbitals, the corresponding density and potential can be found. By inserting the potential into the KS equations we get a shift in the energy and a change in our initial trial orbitals. By repeating this process with our new trial orbitals we will eventually end up with a stable self-consistent solution, which is then the orbitals which gives the correct ground state density.

Chapter 2

Introduction to Exchange-Correlation functionals

The focus of this chapter will be the exchange-correlation (xc) energy functional. We will look at the general properties of the functional, its physical significance and various more and more complicated approximations one can make in order to get an expression for the functional.

In (1.48) we defined the xc energy functional as:

$$E_{xc}[\rho] = F[\rho] - E_H[\rho] - T_s[\rho], \quad (1.48)$$

where the Hohenberg-Kohn (HK) energy functional was defined in (1.19) and extended to N -representable in (1.29):

$$F[\rho] = T[\rho] + W[\rho]. \quad (2.1)$$

By combining (1.48) and (2.1) we get:

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + W[\rho] - E_H[\rho]. \quad (2.2)$$

So the xc energy is the kinetic energy difference between an interacting and non-interacting system, plus the difference between the many-body particle interaction and the Hartree interaction.

The xc energy is often split:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho], \quad (2.3)$$

where the exchange-energy is then given as:

$$E_x[\rho] = W[\rho] - E_H[\rho], \quad (2.4)$$

and the correlation energy as:

$$E_c[\rho] = T[\rho] - T_s[\rho]. \quad (2.5)$$

In general the exchange energy is much easier to calculate than the correlation energy, and since the exchange energy is also normally the largest of the two terms the splitting makes very good sense.

Exchange energy

If we focus on the exchange-energy first, we note that this is nothing more than the standard Hartree-Fock exchange energy, which can be written as¹:

$$E_x[\rho] = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.6)$$

One immediate concern with the above expression, is that the left side is a functional of the density - as it should be in order to fall within the density functional theory (DFT) domain. But we do not know how to express the orbitals on the right side in terms of the density.

It turns out that this is not actually a problem as we shall see in the end of this chapter, but before we get to that we will look at some simpler approximations to the exchange energy.

Correlation energy

Correlation energy is a very loose concept, which unfortunately can be attributed to just about any term or effect a theory fails to account for.

In our case we clearly defined it in (2.5) as the kinetic energy difference between an interacting and non-interacting system. But while the definition is quite simple and somewhat intuitive, a calculation of the correlation energy is unfortunately not so simple. Still it is possible to derive an expression for the correlation-energy. This is done by defining what is known as a coupling integrated correlation-hole density field², $\int_0^1 d\lambda \rho_{c,\lambda}(\mathbf{r}, \mathbf{r}')$. With this the correlation energy can be expressed as:

$$E_c[\rho] = \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \int_0^1 d\lambda \rho_{c,\lambda}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (2.7)$$

¹An example of this calculation is done in [10, p. 385-386], here they calculate the interparticle interaction, $W[\rho]$, which is split in a direct and exchange term, the direct term is exactly the Hartree-energy.

²Loosely speaking, a correlation-hole density field is the hole an electron makes in the surrounding electron cloud by fulfilling Pauli's exclusion principle. A coupling integrated correlation-hole density field, is then average hole the electron makes when you go from non-correlating particles to fully correlating particles. Greater detail can be found in [9] along with a derivation of the correlation energy.

where λ is a coupling strength parameter, such that when $\lambda = 0$ we have the non-interaction KS-system, and when $\lambda = 1$ we have the fully interacting many-body system.

The problem with the correlation term is then that although we can ascribe some physical meaning to the coupling integrated correlation-hole density field, an actual expression for this matrix is not known.

A schematic showing the complexity of the different xc functionals, along with their locality domain is shown in figure 2.1

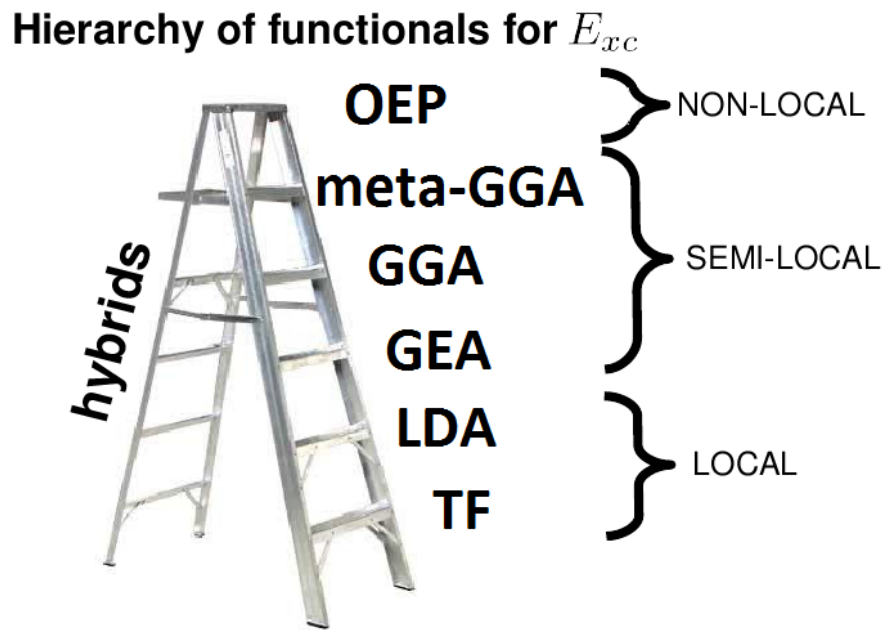


Figure 2.1: The complexity of the different xc-functionals mentioned thus far is shown here.

Adopted from lecture notes by **Esa Räsänen**, University of Jyväskylä, Finland

We now move on to the different kinds of approximations we can use in order to get actual expressions for the exchange-correlation energy functionals.

2.1 Local density approximation

The first and simplest approximation one can make to the xc energy functional, is the local density approximation (LDA). The approximation is called local density approximation because one assumes that the xc functional in a point \mathbf{r} only depends upon the density in \mathbf{r} , which is clearly not the exact xc functional we describe in this way.

In general we can write the xc energy functional using the local density approximation as:

$$E_{xc}^{LDA}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \varepsilon_{xc}(\mathbf{r}), \quad (2.8)$$

where $\varepsilon_{xc}(\rho)$ is the xc energy density. The trick is now to find an expression for the xc energy density.

Some of the earliest and certainly most well known LDA's are the models made by Thomas-Fermi (TF) in 1927[7, 8], which was expanded by Dirac to include exchange contribution in 1930 [11]. We use the word: Model, because that was all TF-models were back then, before DFT was known. But with the formulation of DFT it was a trivial step to turn the TF-model into a rigorous DFT-LDA theory¹.

Today there exists a lot of LDA's, but by far the most successful are the ones build upon the homogeneous electron gas (HEG). We refer to these as HEG-LDA's.

A rigorous derivation of the xc-energy for HEG-LDA can be found in[9]. By splitting in terms of exchange and correlation, the result from a HEG-LDA derivation is:

$$E_x^{LDA}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int d\mathbf{r} \rho^{4/3}(\mathbf{r}), \quad (2.9)$$

which means that the actual exchange-LDA-potential is given as:

$$v_x^{LDA}[\rho](\mathbf{r}) = \frac{\delta E_x^{LDA}}{\delta \rho(\mathbf{r})} = - \left(\frac{3}{\pi} \right)^{1/3} \rho^{1/3}(\mathbf{r}). \quad (2.10)$$

A corresponding analytical expression for the correlation effect is only known in the limit of weak or strong correlation. For the intermediate cases, values of the correlation effect has been calculated using quantum monte carlo simulations. From these simulations people have created interpolated expression, which can accurately describe the local density correlation effect[12].

¹Note that the transformation of the TF-model into a DFT-LDA only gives an approximation to the exchange component and completely neglect the correlation term. From a formal point of view this is of course a problem, but in practice one rarely bothers to calculate the complicated correlation part, since the error on the exchange part due to LDA, is larger than the small correlation correction.

The simple local functionals and in particular LDA was a huge success. The accuracy of the crude approximation was much better than anyone at first expected¹.

¹Upon closer analysis it has been concluded that the primary explanation for LDA's good accuracy stems from the fact that the exchange-correlation-hole in a LDA's fulfil a fundamental sum rule. In simple terms this sum rule states that the hole left by an electron in the surrounding electron cloud, due to Pauli's exclusion principle, should always integrate to minus one.

2.2 Semi-local functionals

The next logical step after local functionals in the search for better approximations to the xc-functional, is semi-local functionals.

By a semi-local functional we mean a functional which not only depends on the variable at the point of interest but also in the neighbouring points. With the neighbouring points included the possibility to include gradients of the variables is unlocked.

Several such gradient methods were investigated and incorporated to various degrees of success.

2.2.1 Gradient expansion approximation

One of the earliest semi-local functionals tried in DFT was the gradient expansion approximation (GEA). GEA is the natural expansion of HEG-LDA. In HEG-LDA one approximates the electron density as $\rho(\mathbf{r}) = \rho_0$. A natural correction would be to consider small variations in the density such that:

$$\rho(\mathbf{r}) = \rho_0 + \delta\rho(\mathbf{r}), \quad (2.11)$$

with the constraint:

$$\int d\mathbf{r} \delta\rho(\mathbf{r}) = 0, \quad (2.12)$$

which ensures an unbiased correction.

By Taylor expanding the xc-energy functional around the homogeneous density ρ_0 one finds:

$$E_{xc} = E_{xc}[\rho_0] + \sum_{m=1}^{\infty} \frac{1}{m!} \int d\mathbf{r}_1 \dots d\mathbf{r}_m \left. \frac{\delta^m E_{xc}}{\delta\rho(\mathbf{r}_1) \dots \delta\rho(\mathbf{r}_m)} \right|_{\rho=\rho_0} \delta\rho(\mathbf{r}_1) \dots \delta\rho(\mathbf{r}_m). \quad (2.13)$$

This is the starting point in deriving GEA, for an in-depth derivation see [13]. The results one gets in the end is:

$$E_x^{GEA}[\rho] = E_x^{LDA}[\rho] + A \int d\mathbf{r} \frac{|\nabla\rho(\mathbf{r})|^2}{\rho^{4/3}(\mathbf{r})} + B \int d\mathbf{r} \frac{|\nabla^2\rho(\mathbf{r})|^2}{\rho^2(\mathbf{r})} + \dots, \quad (2.14)$$

where the first few front factors are known. Once again the correlation energy does not have a simple expression, but the first term in the gradient correlation correction is known[14].

In practice GEA is a disaster. It is a disaster because even though it is an extension of LDA it is less accurate than LDA. This may at first seem counter-intuitive since GEA is LDA plus some corrections. But by introducing the corrections several problems were introduced. The main loss in accuracy stems from the fact that the simple LDA accidentally fulfil the previously mentioned sum rule, whereas GEA does not. This was however not the only problem with GEA. Several

other problems were also introduced by going from LDA to GEA: the correlation energy in GEA has the wrong sign, GEA introduced unphysical oscillations in the xc-functional and broke down in the asymptotic range[15].

The next type of approximations we will look at seeks to correct some of these mistakes.

2.2.2 Generalized gradient approximation

We now move on to the next type of functionals which are still semi-local, but which seeks to fix some of the issues encountered in the earlier GEA. It was identified that the previously mentioned sum rule would be preserved if the exchange-hole, $\rho_x(\mathbf{r}, \mathbf{r}')$, in GEA fulfilled the following criteria:

$$\rho_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) \leq 0, \quad (2.15)$$

$$\int d\mathbf{u} \rho_x(\mathbf{r}, \mathbf{r} + \mathbf{u}) = -1, \quad (2.16)$$

where $\mathbf{u} = \mathbf{r}' - \mathbf{r}$.

Similarly the problems in the correlation energy could be prevented with the following constraint:

$$\int d\mathbf{u} \rho_c(\mathbf{r}, \mathbf{r} + \mathbf{u}) = 0. \quad (2.17)$$

The group of functionals which explicitly fulfill these constraints are called Generalized gradient approximations (GGA). Two different working GGA's emerged after much work. The first was mainly developed by J.Perdew [16, 17]. The second was initially developed by Becke [18], but later corrected by Leeuwen & Baerends [19].

Perdew developed a non-empirical theory by introducing a real-space cutoff into GEA. To be more precise, he fixed the exchange-hole problem by explicitly cutting it off to exactly fit the constraints made in (2.15) and (2.16):

$$\rho_x^{GGA}(\mathbf{r}, \mathbf{r} + \mathbf{u}) = \rho_x^{GEA} \Theta(y) \Theta(R_c(\mathbf{r} - \mathbf{u})), \quad (2.18)$$

where the first stepfunction enforces (2.15), while the cutoff radius R_c is chosen such that (2.16) is satisfied. From this Perdew finds the simple expression for the exchange energy:

$$E_x^{GGA}[\rho] = A_x \int d\mathbf{r} \rho^{4/3} F_x^{GGA}(s(\mathbf{r})), \quad (2.19)$$

where $F_x^{GGA}(s)$ is given as:

$$F_x^{GGA}(s) = \left(1 + \frac{105}{81} s^2 + 14s^4 + \frac{1}{5} s^6 \right)^{1/15}, \quad (2.20)$$

where s is a scaled gradient given as:

$$s = \frac{\nabla\rho(\mathbf{r})}{2k_F\rho(\mathbf{r})}. \quad (2.21)$$

As for the correlation energy, improvements were also made such that (2.17) could be fulfilled.

Becke developed a simple empirical theory. Where he took the lowest-order gradient correction to LDA and patched up the problems it contained.

The starting ground for Becke was the lowest-order gradient correction, which can be uniquely determined from dimensional analysis:

$$E_x^{LGC} = E_x^{LDA} - \beta \int d\mathbf{r} \frac{(\nabla\rho(\mathbf{r}))^2}{\rho^{4/3}(\mathbf{r})}, \quad (2.22)$$

where β is a dimensionless constant.

The primary problem with this energy functional is that the corresponding potential diverges asymptotically in realistic atomic and molecular systems. An early fix to this was to change the functional such that:

$$E_x = E_x^{LDA} - \beta \int d\mathbf{r} \rho^{4/3}(\mathbf{r}) \frac{x^2(\mathbf{r})}{1 + \gamma x^2(\mathbf{r})}, \quad (2.23)$$

where β and γ are fitting constants and $x(\mathbf{r})$ is given as:

$$x(\mathbf{r}) = \frac{|\nabla\rho(\mathbf{r})|}{\rho^{4/3}(\mathbf{r})}. \quad (2.24)$$

With this fix the potential is no longer diverging.

Leeuwen & Baerends could however do even better [19]. It is well known that for any finite system the exchange potential should asymptotically go as¹:

$$\lim_{r \rightarrow \infty} V_x(r) = -\frac{1}{r}. \quad (2.25)$$

With this in mind Leeuwen & Baerends created the model potential known as *LB α 94*[19]:

$$V_x^{LB\alpha94}(\mathbf{r}) = \alpha V_x^{LDA}(\mathbf{r}) + \beta G_x(\mathbf{r}), \quad (2.26)$$

where α and β are fitting constants. $V_x^{LDA}(\mathbf{r})$ is given in (2.10) and $G_x(\mathbf{r})$ is the gradient correction given as:

$$G_x(\mathbf{r}) = \frac{x^2(\mathbf{r})\rho^{1/3}(\mathbf{r})}{1 + 3\beta x(\mathbf{r}) \sinh^{-1}[x(\mathbf{r})]}, \quad (2.27)$$

¹The asymptotic behaviour can physically be explained as follows: We know that the exchange functional corresponds to a hole in the electron cloud, further we know from the sum rule that the sum hole should sum up to minus one. But in the asymptotic region we can consider this smeared out electron hole as a point particle and we know the asymptotic potential of an electron goes as $1/r$.

with $x(\mathbf{r})$ in (2.24).

Here, a quick side note is in order before we move on. Originally this was the potential we planned to numerically implement. But as we learned during the implementation, not every potential is suited for numerical implementation in a spherical harmonic basis. Hence we eventually had to scrap the *LB α 94* potential and move on to another potential more suitable for spherical harmonic conversion¹.

We have seen examples of GGA's. If one wants even better approximations there are several ways to do this. The obvious natural way is to include higher order terms, but this is usually not the best way to go. Instead one usually make what is known as meta-GGA's.

meta-GGA's

The idea with Meta-GGA's is to include a functional dependence on the Kohn-Sham kinetic energy:

$$E_{xc}^{mGGA}[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), T(\mathbf{r})] \quad , \quad T(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla\varphi_i(\mathbf{r})|^2. \quad (2.28)$$

So our xc-energy functional now not only depends upon the density and the gradient of the density, but an additional parameter. The introduction of a new variable not explicitly depending upon the density warrant us to question whether we are still within the DFT domain. In order to see that this is indeed the case we exploit the fact that the kinetic energy is a functional of the orbitals, and through DFT we know that the orbitals are uniquely determined by the density, hence the kinetic energy is also uniquely determined by the density. We say that the kinetic energy is an implicit functional of the density. By introducing another parameter the number of constraints which the functional can fulfil gets larger, while the numerical cost stays relatively low.

It turns out that meta-GGA's are just one example of a much broader type of functionals known as hybrid functionals which in general takes us into the domain of non-local functionals.

¹The implementation problems are twofold. The first problem is in the fraction powers which the density is taken to. Because of these fractions we end up with a fraction spherical harmonic basis. This fraction spherical harmonic basis can be converted to a regular spherical harmonic basis using the technique discussed in appendix C, but this technique is both very expensive and quite inaccurate.

The other problem is, in order to make sense of the denominator we need to express $x(\mathbf{r})$ as a regular number. Doing this requires a switching from spherical harmonic basis to angular grid points.

2.3 Non-local functionals

We now turn to the final type of functionals, namely the non-local functionals. non-local functionals depends upon parameters anywhere in space. An example of such a non-local functional will be shown in the next chapter, where we derive the optimised effective potential, but before we get to that a few words about hybrid functionals are in order for the sake of completeness.

2.3.1 Hybrid functionals

A hybrid functional is a functional which both explicitly and implicitly depends upon the density.

The functional dependence upon the density can be illustrated as follows:

$$\rho(\mathbf{r}) \xrightarrow{DFT} V_{KS}[\rho] \xrightarrow{KS} \{\varphi_i[V_{KS}[\rho]], \varepsilon_i[V_{KS}[\rho]]\} \quad (2.29)$$

where φ_i is the Kohn-Sham orbitals and ε_i the corresponding eigenenergies.

From this we see that a hybrid functional is not necessarily a non-local functional¹.

In general a hybrid functional usually stems from a linear combination of an orbital dependent Hartree-Fock exchange potential, and any number of explicit density dependent xc-functionals². The problematic thing about hybrid potentials is to find the linear coefficients. Usually this is done by optimizing the functional to a certain set of systems, which makes the functional semi-empirical.

An example of a series of very successful hybrid functional are made by Becke and started with [20], these combine the Hartree-Fock exchange potential with the LDA xc-functional:

$$E_{xc}^{\text{Becke}} = c_0 E_x[\rho] + c_1 E_{xc}^{\text{LDA}}[\rho]. \quad (2.30)$$

This functional has later been improved to include several other explicit density functionals. By including sufficient terms and optimizing the fitting parameters these hybrid functionals are capable of obtaining very good results for a large variety of systems including molecular systems. But due to their empirical nature and lack of physical insight, these functionals should not push DFT into new domains.

¹The meta-GGA's were semi-local functionals but as we can see from the definition of hybrid functionals, the meta-GGA's are also hybrid functionals.

²The reason why these functionals are called hybrid, is because they combine different functionals into a new one

Chapter 3

Orbital Exchange-Correlation functionals

In the beginning of the last chapter we noted that an exact expression for the xc-energy could be found as:

$$E_x[\rho] = -\frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \int d\mathbf{r} d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad (2.6)$$

$$E_c[\rho] = \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}) \int_0^1 d\lambda \rho_{c,\lambda}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (2.7)$$

The reason why we did not do any further work on these expressions then, was because we were limited to functionals explicitly density dependent. This limitation ended when we introduced implicit density dependence at the end of last chapter.

The xc-potential found from the exact xc energy functional is called the optimised effective potential (OEP). The only problem with the OEP is that the final expression is an integral equation, which is very expensive to solve numerically speaking. Luckily there exists an approximation to OEP, called the KLI-approximation¹, which removes the integral without much loss in accuracy[21].

In the following we will ignore the correlation effect and only focus on the exchange term.

¹Named after its 3 founding fathers: J.B. Krieger, Yan Li & G.J. Iafrate.

3.1 Introduction to optimised effective potential

Our starting point is the exchange potential, which we know is related to its corresponding energy functional as:

$$v_x^{OEP}(\mathbf{r}) = \frac{\delta E_x[\varphi]}{\delta \rho(\mathbf{r})}. \quad (3.1)$$

We want to find an expression for v_x^{OEP} , but finding the derivative of the exchange energy, as given in (2.6), with regard to the density is nontrivial. Instead what one does is to invoke the chain rule¹:

$$\begin{aligned} v_x^{OEP}(\mathbf{r}) &= \frac{\delta E_x[\varphi]}{\delta \rho(\mathbf{r})} \\ &= \int d\mathbf{r}' \frac{\delta E_x[\varphi]}{\delta v_s(\mathbf{r}')} \frac{\delta v_s(\mathbf{r}')}{\delta \rho(\mathbf{r})}, \end{aligned} \quad (3.2)$$

where v_s is the Kohn-Sham (KS) single particle potential.

We invoke the chain rule once again:

$$v_x^{OEP}(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \int d\mathbf{r}'' \left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}'')} \frac{\delta \varphi_{i\sigma}(\mathbf{r}'')}{\delta v_s(\mathbf{r}')} \frac{\delta v_s(\mathbf{r}')}{\delta \rho(\mathbf{r})} + c.c. \right\}, \quad (3.3)$$

note that we got a complex conjugate part, because the orbitals are in general complex objects.

We define the response function of the density with regard to the potential in the normal way:

$$\chi_s(\mathbf{r}, \mathbf{r}') = \frac{\delta \rho(\mathbf{r})}{\delta v_s(\mathbf{r}')}, \quad (3.4)$$

and note that the last term in the OEP-equation is the inverse response function:

$$v_x^{OEP}(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \int d\mathbf{r}'' \left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}'')} \frac{\delta \varphi_{i\sigma}(\mathbf{r}'')}{\delta v_s(\mathbf{r}')} \chi_s^{-1}(\mathbf{r}, \mathbf{r}') + c.c. \right\}. \quad (3.5)$$

¹A detailed mathematical explanation of how the chain rule works on functionals can be found in [9, p. 246-254].

This equation is multiplied with $\chi_s(\mathbf{r}, \mathbf{r}''')$ and integrated, which gives us:

$$\begin{aligned} \int d\mathbf{r} \chi_s(\mathbf{r}, \mathbf{r}''') v_x^{OEP}(\mathbf{r}) &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \int d\mathbf{r}'' \\ &\left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_i(\mathbf{r}'')} \frac{\delta \varphi_i(\mathbf{r}'')}{\delta v_s(\mathbf{r}')} \frac{\chi_s(\mathbf{r}, \mathbf{r}''')}{\chi_s(\mathbf{r}, \mathbf{r}')} + c.c. \right\} \\ &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \int d\mathbf{r}'' \\ &\left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_i(\mathbf{r}'')} \frac{\delta \varphi_i(\mathbf{r}'')}{\delta v_s(\mathbf{r}')} \frac{\delta v_s(\mathbf{r}')}{\delta v_s(\mathbf{r}''')} + c.c. \right\}, \end{aligned} \quad (3.6)$$

Taking the variation of a variable with regards to two independent coordinates gives nothing. Hence we get a delta-function:

$$\begin{aligned} \int d\mathbf{r} \chi_s(\mathbf{r}, \mathbf{r}''') v_x^{OEP}(\mathbf{r}) &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \int d\mathbf{r}'' \\ &\left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_i(\mathbf{r}'')} \frac{\delta \varphi_i(\mathbf{r}'')}{\delta v_s(\mathbf{r}')} \delta(\mathbf{r}' - \mathbf{r}''') + c.c. \right\} \\ &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}'' \left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_i(\mathbf{r}'')} \frac{\delta \varphi_i(\mathbf{r}'')}{\delta v_s(\mathbf{r}''')} + c.c. \right\}. \end{aligned} \quad (3.7)$$

Finally we rename the variables:

$$\int d\mathbf{r}' \chi_s(\mathbf{r}', \mathbf{r}) v_x^{OEP}(\mathbf{r}') = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \right\}. \quad (3.8)$$

The above integral equation is a very common starting point in deriving the optimised effective potential, the job is now to express the three unknown components in terms of: The density, the KS orbitals and their corresponding eigenenergies.

term 1 - $\frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}'')}$

We start with the easy term $\frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}'')}$. This term is rather straightforward because the Hartree-Fock exchange energy explicitly contains the wavefunction and no other terms in the functional implicitly contains it.

$$\begin{aligned} \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}'')} &= -\frac{1}{2} \sum_{\sigma'} \sum_{k,j} \int d\mathbf{r} \int d\mathbf{r}' \left\{ \frac{\varphi_{k\sigma'}^*(\mathbf{r}) \varphi_{j\sigma'}^*(\mathbf{r}') \varphi_{j\sigma'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \frac{\delta \varphi_{k\sigma'}(\mathbf{r}')}{\delta \varphi_{i\sigma}(\mathbf{r}'')} \right. \\ &\quad \left. + \frac{\varphi_{k\sigma}^*(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{\delta \varphi_{j\sigma'}(\mathbf{r}')}{\delta \varphi_{i\sigma}(\mathbf{r}'')} \right\}. \end{aligned} \quad (3.9)$$

Different orbitals are, like different wavefunctions, considered completely independent. Hence we only get a contribution from the last term, if $j = i$, $\sigma = \sigma'$ and $\mathbf{r}' = \mathbf{r}''$. Written as delta-functions we get:

$$\begin{aligned}
\frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}'')} &= -\frac{1}{2} \sum_{\sigma'} \sum_{k,j} \int d\mathbf{r} \int d\mathbf{r}' \left\{ \frac{\varphi_{k\sigma'}^*(\mathbf{r}) \varphi_{j\sigma'}^*(\mathbf{r}') \varphi_{j\sigma'}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \delta_{ki} \delta(\mathbf{r}' - \mathbf{r}'') \delta_{\sigma\sigma'} \right. \\
&\quad \left. + \frac{\varphi_{k\sigma'}^*(\mathbf{r}) \varphi_{j\sigma'}^*(\mathbf{r}') \varphi_{k\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \delta_{ji} \delta(\mathbf{r} - \mathbf{r}'') \delta_{\sigma\sigma'} \right\} \\
&= -\frac{1}{2} \sum_{k,j} \left\{ \int d\mathbf{r} \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}'') \varphi_{j\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}''|} \right. \\
&\quad \left. + \int d\mathbf{r}' \frac{\varphi_{k\sigma}^*(\mathbf{r}'') \varphi_{i\sigma}^*(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r}')}{|\mathbf{r}'' - \mathbf{r}'|} \right\}.
\end{aligned} \tag{3.10}$$

By changing the coordinate notation in the first term, and the summation symbol in the second we get:

$$\begin{aligned}
\frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}'')} &= -\frac{1}{2} \sum_j \left\{ \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}^*(\mathbf{r}'') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \right. \\
&\quad \left. + \int d\mathbf{r}' \frac{\varphi_{j\sigma}^*(\mathbf{r}'') \varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}'' - \mathbf{r}'|} \right\}.
\end{aligned} \tag{3.11}$$

Note that the orbitals are just numbers, hence they commute. This enables us to contract the two terms to one:

$$\frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}'')} = - \sum_j \varphi_{j\sigma}^*(\mathbf{r}'') \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|}. \tag{3.12}$$

For completeness we also write out the complex conjugate:

$$\frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}^*(\mathbf{r}'')} = - \sum_j \varphi_{j\sigma}(\mathbf{r}'') \int d\mathbf{r}' \frac{\varphi_{j\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|}. \tag{3.13}$$

We now have an expression for the first term.

term 2 - $\frac{\delta \varphi_{i\sigma}(\mathbf{r}'')}{\delta v_s(\mathbf{r}'')}$

Next we take the middle term, which is $\frac{\delta \varphi_{i\sigma}(\mathbf{r}'')}{\delta v_s(\mathbf{r}'')}$. This term contains v_s which is the KS potential, hence in order to calculate this term we will have to start with an equation which connects the orbitals and the KS potential. The equation that does this is the KS equation as defined in (1.41), which will be our starting point:

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + v_s(\mathbf{r}, t) \right] \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_i \varphi_{i\sigma}(\mathbf{r}), \quad i = \{1, \dots, N_\sigma\}. \tag{1.41}$$

To shorten the notation we introduce $h_s(\mathbf{r}) = -\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_s(\mathbf{r})$, by using this we can rewrite (1.41) as:

$$\begin{aligned} h_s(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}) &= \varepsilon_i\varphi_{i\sigma}(\mathbf{r}) \\ \Rightarrow 0 &= [h_s(\mathbf{r}) - \varepsilon_i]\varphi_{i\sigma}(\mathbf{r}). \end{aligned} \quad (3.14)$$

Our goal is to find how the wavefunction change under an infinitesimal variation in the potential, hence we introduce such an infinitesimal variation in the potential:

$$v_s(\mathbf{r}) \rightarrow v_s(\mathbf{r}) + \delta v_s(\mathbf{r}), \quad (3.15)$$

this change give rise to a shift in the eigenvalues and orbitals:

$$\varepsilon_i \rightarrow \varepsilon_i + \delta\varepsilon_i, \quad \varphi_{i\sigma}(\mathbf{r}) \rightarrow \varphi_{i\sigma}(\mathbf{r}) + \delta\varphi_{i\sigma}(\mathbf{r}). \quad (3.16)$$

This will change the KS equation to the following:

$$\begin{aligned} 0 &= [h_s(\mathbf{r}) + \delta v_s(\mathbf{r}) - \varepsilon_i - \delta\varepsilon_i][\varphi_{i\sigma}(\mathbf{r}) + \delta\varphi_{i\sigma}(\mathbf{r})] \\ &= [h_s(\mathbf{r}) + \delta v_s(\mathbf{r}) - \varepsilon_i - \delta\varepsilon_i]\varphi_{i\sigma}(\mathbf{r}) + [h_s(\mathbf{r}) + \delta v_s(\mathbf{r}) - \varepsilon_i - \delta\varepsilon_i]\delta\varphi_{i\sigma}(\mathbf{r}). \end{aligned} \quad (3.17)$$

By using the unmodified KS equation and its infinitesimal counterpart, several terms can be eliminated from the above modified KS equation. After elimination we end up with:

$$0 = [\delta v_s(\mathbf{r}) - \delta\varepsilon_i]\varphi_{i\sigma}(\mathbf{r}) + [h_s(\mathbf{r}) - \varepsilon_i]\delta\varphi_{i\sigma}(\mathbf{r}), \quad (3.18)$$

and by moving the terms we get:

$$[\delta v_s(\mathbf{r}) - \delta\varepsilon_i]\varphi_{i\sigma}(\mathbf{r}) = [\varepsilon_i - h_s(\mathbf{r})]\delta\varphi_{i\sigma}(\mathbf{r}). \quad (3.19)$$

Next we use the fact that the orbitals form a complete set, hence anything can be expressed by them. In particular the variation in the orbital can be expressed by the orbitals:

$$\delta\varphi_{i\sigma}(\mathbf{r}) = \sum_{k=1}^{\infty} c_k^i \varphi_{k\sigma}(\mathbf{r}). \quad (3.20)$$

We insert (3.20) in (3.19):

$$\begin{aligned} [\delta v_s(\mathbf{r}) - \delta\varepsilon_i]\varphi_{i\sigma}(\mathbf{r}) &= [\varepsilon_i - h_s(\mathbf{r})] \sum_{k=1}^{\infty} c_k^i \varphi_{k\sigma}(\mathbf{r}) \\ &= \sum_{k=1}^{\infty} c_k^i [\varepsilon_i - h_s(\mathbf{r})] \varphi_{k\sigma}(\mathbf{r}). \end{aligned} \quad (3.21)$$

Finally we once again use the KS equation on the last term, which gives:

$$[\delta v_s(\mathbf{r}) - \delta \varepsilon_i] \varphi_{i\sigma}(\mathbf{r}) = \sum_{k=1}^{\infty} c_k^i [\varepsilon_i - \varepsilon_k] \varphi_{k\sigma}(\mathbf{r}). \quad (3.22)$$

We multiply (3.22) with $\varphi_{j\sigma}^*(\mathbf{r})$ and integrate over r :

$$\int d\mathbf{r} \varphi_{j\sigma}^*(\mathbf{r}) [\delta v_s(\mathbf{r}) - \delta \varepsilon_i] \varphi_{i\sigma}(\mathbf{r}) = \int d\mathbf{r} \varphi_{j\sigma}^*(\mathbf{r}) \sum_{k=1}^{\infty} c_k^i [\varepsilon_i - \varepsilon_k] \varphi_{k\sigma}(\mathbf{r}), \quad (3.23)$$

which when changed to Dirac notation can be written as:

$$\langle \varphi_{j\sigma} | \delta v_s | \varphi_{i\sigma} \rangle - \langle \varphi_{j\sigma} | \delta \varepsilon_i | \varphi_{i\sigma} \rangle = \sum_{k=1}^{\infty} c_k^i \langle \varphi_{j\sigma} | \varepsilon_i - \varepsilon_k | \varphi_{k\sigma} \rangle. \quad (3.24)$$

Next the facts that the eigenvalues are independent of r and that the orbitals are orthogonal on each other, are used:

$$\begin{aligned} \Rightarrow \langle \varphi_{j\sigma} | \delta v_s | \varphi_{i\sigma} \rangle - \delta \varepsilon_i \delta_{ji} &= \sum_{k=1}^{\infty} c_k^i [\varepsilon_i - \varepsilon_k] \delta_{jk} \\ &= c_j^i [\varepsilon_i - \varepsilon_j]. \end{aligned} \quad (3.25)$$

We now have two different cases to consider, either $i = j$ or $i \neq j$. We consider each separately.

If $i = j$ we get:

$$\begin{aligned} \Rightarrow \langle \varphi_{i\sigma} | \delta v_s | \varphi_{i\sigma} \rangle - \delta \varepsilon_i &= 0 \\ \Rightarrow \delta \varepsilon_i &= \langle \varphi_{i\sigma} | \delta v_s | \varphi_{i\sigma} \rangle, \end{aligned} \quad (3.26)$$

by returning to normal notation we get:

$$\begin{aligned} \delta \varepsilon_i &= \int d\mathbf{r} |\varphi_{i\sigma}(\mathbf{r})|^2 \delta v_s(\mathbf{r}) \\ \Rightarrow \frac{\delta \varepsilon_i}{\delta v_s(\mathbf{r})} &= |\varphi_{i\sigma}(\mathbf{r})|^2. \end{aligned} \quad (3.27)$$

We knew that a change in the potential would induce a density dependent change in the energy, but now we have an explicit expression for this change.

With the special case $i = j$ taken care of, we can move on to the case which we need in order to construct the OEP.

If $i \neq j$ we get:

$$\begin{aligned} \langle \varphi_{j\sigma} | \delta v_s | \varphi_{i\sigma} \rangle &= c_j^i [\varepsilon_i - \varepsilon_j] \\ \Rightarrow c_j^i &= \frac{\langle \varphi_{j\sigma} | \delta v_s | \varphi_{i\sigma} \rangle}{\varepsilon_i - \varepsilon_j}. \end{aligned} \quad (3.28)$$

The only expansion coefficient we do not have now, is for $i = j$. Without knowing the coefficient for $i = j$ we can write (3.20) as the following:

$$\begin{aligned}\delta\varphi_{i\sigma}(\mathbf{r}) &= \sum_{j=1}^{\infty} c_j^i \varphi_{j\sigma}(\mathbf{r}) \\ &= c_i^i \varphi_{i\sigma}(\mathbf{r}) + \sum_{j \neq i}^{\infty} \frac{\langle \varphi_{j\sigma} | \delta v_s | \varphi_{i\sigma} \rangle}{\varepsilon_i - \varepsilon_j} \varphi_{j\sigma}(\mathbf{r}).\end{aligned}\quad (3.29)$$

In order to determine c_i^i , we use the fact that $\delta v_s(\mathbf{r}) = 0 \Rightarrow \delta\varphi_{i\sigma}(\mathbf{r}) = 0$.

So assume that $\delta v_s(\mathbf{r}) = 0$, we then get:

$$\begin{aligned}0 &= \delta\varphi_{i\sigma}(\mathbf{r}) \\ &= c_i^i \varphi_{i\sigma}(\mathbf{r}) + \sum_{j \neq i}^{\infty} \frac{\langle \varphi_{j\sigma} | \varphi_{i\sigma} \rangle}{\varepsilon_i - \varepsilon_j} \varphi_{j\sigma}(\mathbf{r}) \\ &= c_i^i \varphi_{i\sigma}(\mathbf{r}).\end{aligned}\quad (3.30)$$

If we disregard the trivial case where the orbital is zero everywhere, we necessarily get that:

$$c_i^i = 0. \quad (3.31)$$

When this is inserted into (3.29) we get:

$$\delta\varphi_{i\sigma}(\mathbf{r}) = \sum_{j \neq i}^{\infty} \frac{\langle \varphi_{j\sigma} | \delta v_s | \varphi_{i\sigma} \rangle}{\varepsilon_i - \varepsilon_j} \varphi_{j\sigma}(\mathbf{r}), \quad (3.32)$$

by returning from Dirac notation we get:

$$\begin{aligned}\delta\varphi_{i\sigma}(\mathbf{r}) &= \sum_{j \neq i}^{\infty} \frac{\varphi_{j\sigma}(\mathbf{r})}{\varepsilon_i - \varepsilon_j} \int d\mathbf{r}' \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') \delta v_s(\mathbf{r}') \\ &= - \int d\mathbf{r}' \sum_{j \neq i}^{\infty} \frac{\varphi_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}')}{\varepsilon_j - \varepsilon_i} \varphi_{i\sigma}(\mathbf{r}') \delta v_s(\mathbf{r}') \\ &= - \int d\mathbf{r}' G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') \delta v_s(\mathbf{r}'),\end{aligned}\quad (3.33)$$

where we defined the Green's function:

$$G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i}^{\infty} \frac{\varphi_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}')}{\varepsilon_j - \varepsilon_i}. \quad (3.34)$$

Note the relation between the Green's function and its complex conjugate:

$$G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') = G_{s,i\sigma}^*(\mathbf{r}', \mathbf{r}). \quad (3.35)$$

By making a variation in the KS potential in (3.33) we get:

$$\begin{aligned}\frac{\delta\varphi_{i\sigma}(\mathbf{r})}{\delta v_s(\mathbf{r}')} &= - \int d\mathbf{r}' G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') \frac{\delta v_s(\mathbf{r}')}{\delta v_s(\mathbf{r}')} \\ &= - \int d\mathbf{r}' G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}') \\ &= -G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}(\mathbf{r}')\end{aligned}\quad (3.36)$$

A quick renaming of variables yields us the desired result:

$$\frac{\delta\varphi_{i\sigma}(\mathbf{r})}{\delta v_s(\mathbf{r}')} = -G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}(\mathbf{r}'). \quad (3.37)$$

For completeness we also write out the complex conjugate:

$$\frac{\delta\varphi_{i\sigma}^*(\mathbf{r})}{\delta v_s(\mathbf{r}')} = -G_{s,i\sigma}^*(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}'). \quad (3.38)$$

term 3 - $\chi_s(\mathbf{r}', \mathbf{r})$

The response function was defined in (3.4) as:

$$\chi_s(\mathbf{r}, \mathbf{r}') = \frac{\delta\rho(\mathbf{r})}{\delta v_s(\mathbf{r}')} \quad (3.4)$$

We now seek to express the response function in terms of the orbitals. To do this, we insert the relation between density and orbitals as given in (1.42):

$$\begin{aligned}\chi_s(\mathbf{r}, \mathbf{r}') &= \frac{\delta}{\delta v_s(\mathbf{r}')} \left[\sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\varphi_{i\sigma}(\mathbf{r})|^2 \right] \\ &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \left[\varphi_{i\sigma}^*(\mathbf{r}) \frac{\delta\varphi_{i\sigma}(\mathbf{r})}{\delta v_s(\mathbf{r}')} + \varphi_{i\sigma}(\mathbf{r}) \frac{\delta\varphi_{i\sigma}^*(\mathbf{r})}{\delta v_s(\mathbf{r}')} \right].\end{aligned}\quad (3.39)$$

The variations which we have in the above expression are exactly the terms which we just calculated in (3.37) & (3.38). By insertion we get:

$$\begin{aligned}\chi_s(\mathbf{r}, \mathbf{r}') &= - \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \left[\varphi_{i\sigma}^*(\mathbf{r}) G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') + \varphi_{i\sigma}(\mathbf{r}) G_{s,i\sigma}^*(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}') \right] \\ &= - \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \varphi_{i\sigma}^*(\mathbf{r}) G_{s,i\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{i\sigma}(\mathbf{r}') + c.c..\end{aligned}\quad (3.40)$$

Note that the terms we are actually interested in has \mathbf{r} & \mathbf{r}' switched, if we do this we get:

$$\chi_s(\mathbf{r}', \mathbf{r}) = - \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \varphi_{i\sigma}^*(\mathbf{r}') G_{s,i\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) + c.c.. \quad (3.41)$$

This was the last of the three terms we needed in order to make the OEP.

3.2 Making the optimised effective potential

As a reminder, our initial equation was given in (3.8) as the following:

$$\int d\mathbf{r}' \chi_s(\mathbf{r}', \mathbf{r}) v_x^{OEP}(\mathbf{r}') = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}')} \frac{\delta \varphi_{i\sigma}(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \right\}. \quad (3.8)$$

By inserting (3.37) & (3.41) into (3.8) we get:

$$\begin{aligned} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' v_x^{OEP}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}') G_{s,i\sigma}(\mathbf{r}', \mathbf{r}) \varphi_i(\mathbf{r}) + c.c. = \\ - \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \left\{ \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}')} G_{s,i\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) + c.c. \right\}. \end{aligned} \quad (3.42)$$

We collect the terms on the same side, and pull out some factors:

$$\begin{aligned} 0 &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \varphi_{i\sigma}^*(\mathbf{r}') \left[v_x^{OEP}(\mathbf{r}') - \frac{1}{\varphi_{i\sigma}^*(\mathbf{r}')} \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}')} \right] G_{s,i\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) + c.c. \\ &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \varphi_{i\sigma}^*(\mathbf{r}') \left[v_x^{OEP}(\mathbf{r}') - u_{x,i\sigma}(\mathbf{r}') \right] G_{s,i\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) + c.c.. \end{aligned} \quad (3.43)$$

where we defined the shorthand notation:

$$u_{x,i\sigma}(\mathbf{r}') = \frac{1}{\varphi_{i\sigma}^*(\mathbf{r}')} \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r}')} \quad (3.44)$$

(3.43) is one way to write the OEP, a shorter expression can be found by defining an orbital shift:

$$\tilde{\varphi}_{i\sigma}^*(\mathbf{r}) := \int d\mathbf{r}' \varphi_{i\sigma}^*(\mathbf{r}') \left[v_x^{OEP}(\mathbf{r}') - u_{x,i\sigma}(\mathbf{r}') \right] G_{s,i\sigma}(\mathbf{r}', \mathbf{r}). \quad (3.45)$$

By introducing the orbital shift to (3.43) we get:

$$0 = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} [\tilde{\varphi}_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) + c.c.]. \quad (3.46)$$

This is also the OEP equation, but now written in a much shorter form. OEP is made from the exact exchange functional and by use of the variational principle in the making we know that this potential will minimize the energy of the system.

The above is the exact exchange energy potential, but unfortunately it is too expensive to calculate in most cases, due to its integral form. In order to fix this we make the KLI-approximation.

3.3 KLI approximation

During the construction of OEP we defined the Green's function:

$$G_{s,i\sigma}(\mathbf{r}', \mathbf{r}) = \sum_{j \neq i}^{\infty} \frac{\varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}')}{\varepsilon_j - \varepsilon_i}. \quad (3.47)$$

What we have here is a sum over all occupied and unoccupied orbital states with their respective eigenenergies.

The KLI-approximation consists of fixating the eigenenergy differences¹. So by assuming the KLI approximation we get the following:

$$\begin{aligned} G_{s,i\sigma}^{KLI}(\mathbf{r}', \mathbf{r}) &= \sum_{j \neq i}^{\infty} \frac{\varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}')}{\Delta} \\ &= \frac{1}{\Delta} \sum_{j \neq i}^{\infty} \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}'). \end{aligned} \quad (3.48)$$

We rewrite the sum and use the completeness relation of the orbitals to get:

$$\begin{aligned} G_{s,i\sigma}^{KLI}(\mathbf{r}', \mathbf{r}) &= \frac{1}{\Delta} \sum_{j=1}^{\infty} \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}') - \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}') \\ &= \frac{1}{\Delta} \delta(\mathbf{r} - \mathbf{r}') - \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}'). \end{aligned} \quad (3.49)$$

By inserting the KLI modified Green's function (3.49) into the OEP equation (3.43), we get:

$$\begin{aligned} 0 &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \varphi_{i\sigma}^*(\mathbf{r}') \left[v_x^{KLI}(\mathbf{r}') - u_{x,i\sigma}(\mathbf{r}') \right] G_{s,i\sigma}^{KLI}(\mathbf{r}', \mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) + c.c. \\ &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int d\mathbf{r}' \varphi_{i\sigma}^*(\mathbf{r}') \left[v_x^{KLI}(\mathbf{r}') - u_{x,i\sigma}(\mathbf{r}') \right] \\ &\quad \frac{1}{\Delta} \left[\delta(\mathbf{r} - \mathbf{r}') - \varphi_{i\sigma}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}) \right] \varphi_{i\sigma}(\mathbf{r}) + c.c.. \end{aligned} \quad (3.50)$$

Δ is multiplied out, and we expand the brackets and use the delta-

¹Actually the KLI approximation is a long and very careful analysis of how one can make a good approximation to the OEP, which in the end turns out to be equivalent to the simple step of approximating the Green's functions like we do [22].

function in the first term to terminate the integral:

$$0 = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \left\{ \varphi_{i\sigma}^*(\mathbf{r}) \left[v_x^{KLI}(\mathbf{r}) - u_{x,i\sigma}(\mathbf{r}) \right] \varphi_{i\sigma}(\mathbf{r}) - \int d\mathbf{r}' \varphi_{i\sigma}^*(\mathbf{r}') \left[v_x^{KLI}(\mathbf{r}') - u_{x,i\sigma}(\mathbf{r}') \right] \varphi_{i\sigma}(\mathbf{r}') \varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \right\} + c.c.. \quad (3.51)$$

The orbitals and their complex conjugates are turned into single particle spin-densities:

$$0 = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \left\{ \rho_{i\sigma}(\mathbf{r}) \left[v_x^{KLI}(\mathbf{r}) - u_{x,i\sigma}(\mathbf{r}) \right] - \rho_{i\sigma}(\mathbf{r}) \int d\mathbf{r}' \varphi_{i\sigma}^*(\mathbf{r}') \left[v_x^{KLI}(\mathbf{r}') - u_{x,i\sigma}(\mathbf{r}') \right] \varphi_{i\sigma}(\mathbf{r}') \right\} + c.c.. \quad (3.52)$$

To shorten the expression once again, we define the spatial average of a function, $X(\mathbf{r})$, as:

$$\langle X \rangle_{i\sigma} = \int d\mathbf{r} \varphi_{i\sigma}^*(\mathbf{r}) X(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}). \quad (3.53)$$

From this definition we get the mean potentials:

$$\langle v_x^{KLI} \rangle_{i\sigma} = \int d\mathbf{r} \varphi_{i\sigma}^*(\mathbf{r}) v_x^{KLI}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \quad (3.54)$$

$$\langle u_{x,i\sigma} \rangle_{i\sigma} = \int d\mathbf{r} \varphi_{i\sigma}^*(\mathbf{r}) u_{x,i\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}). \quad (3.55)$$

Which we can directly insert into (3.52) to get:

$$\begin{aligned} 0 &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \left\{ \rho_{i\sigma}(\mathbf{r}) \left[v_x^{KLI}(\mathbf{r}) - u_{x,i\sigma}(\mathbf{r}) \right] - \rho_{i\sigma}(\mathbf{r}) \left[\langle v_x^{KLI} \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} \right] \right\} \\ &+ c.c.. \\ &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) \left\{ v_x^{KLI}(\mathbf{r}) - u_{x,i\sigma}(\mathbf{r}) - \langle v_x^{KLI} \rangle_{i\sigma} + \langle u_{x,i\sigma} \rangle_{i\sigma} \right\} + c.c.. \end{aligned} \quad (3.56)$$

Now we need to isolate the KLI potential. We start by moving the rest of the terms to the other side of the equation, which gives us:

$$\begin{aligned} v_x^{KLI}(\mathbf{r}) 2 \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) \left[u_{x,i\sigma}(\mathbf{r}) + \langle v_x^{KLI} \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} \right] \\ &+ c.c.. \end{aligned} \quad (3.57)$$

We then use the fact that $\sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) = \rho(\mathbf{r})$, and divide both sides by two times the total density:

$$v_x^{KLI}(\mathbf{r}) = \frac{1}{2\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) \left[u_{x,i\sigma}(\mathbf{r}) + \langle v_x^{KLI} \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} \right] + c.c.. \quad (3.58)$$

We now have an expression for the KLI-potential, which we split in two terms:

$$\begin{aligned} v_x^{KLI}(\mathbf{r}) &= \frac{1}{2\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) [u_{x,i\sigma}(\mathbf{r})] \\ &+ \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \frac{\rho_{i\sigma}(\mathbf{r})}{2\rho(\mathbf{r})} \left[\langle v_x^{KLI} \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} \right] + c.c. \\ &= V_x^S(\mathbf{r}) + V_x^R(\mathbf{r}). \end{aligned} \quad (3.59)$$

The usual saying is that we have split the KLI-potential in a screening and a screening-response potential. The screening potential is always present in any multi electron system, it is the one which contains the asymptotic $1/r$ form which we know any realistic exchange potential must have.

The screening-response potential is a short range potential, it is only present in multi orbital systems and it contains clear clues about the structure of the system.

One very important fact to remember in any actual implementation of this is that any exchange interaction is limited to particles with identical spin. So even though the total exchange potential is the one written in (3.59) the actual orbitals in the system is only going to feel a part of this potential, namely the part which stems from particles of identical spin as themselves.

In (3.59) we introduced the screening and screening-response potential in very compact form. We now expand these expressions in terms of the density and orbitals:

3.3.1 KLI-screening potential

The screening potential was given as:

$$\begin{aligned} V_x^S(\mathbf{r}) &= \frac{1}{2\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) [u_{x,i\sigma}(\mathbf{r}) + c.c.] \\ &= \frac{1}{\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) \Re \{ u_{x,i\sigma}(\mathbf{r}) \}. \end{aligned} \quad (3.60)$$

In (3.44) we defined $u_{x,i\sigma}(\mathbf{r})$, when inserted into the above we get:

$$V_x^S(\mathbf{r}) = \frac{1}{\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \rho_{i\sigma}(\mathbf{r}) \Re \left\{ \frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r})} \right\}. \quad (3.61)$$

We know that the single particle spin density is real, hence we can freely drag it into the real part and then convert it to orbitals:

$$\begin{aligned} V_x^S(\mathbf{r}) &= \frac{1}{\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \Re \left\{ \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r})}{\varphi_{i\sigma}^*(\mathbf{r})} \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r})} \right\} \\ &= \frac{1}{\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \Re \left\{ \varphi_{i\sigma}(\mathbf{r}) \frac{\delta E_x[\varphi]}{\delta \varphi_{i\sigma}(\mathbf{r})} \right\}. \end{aligned} \quad (3.62)$$

Next we finally use the expression which we found in (3.12):

$$\begin{aligned} V_x^S(\mathbf{r}) &= -\frac{1}{\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \Re \left\{ \varphi_{i\sigma}(\mathbf{r}) \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\} \\ &= -\frac{1}{\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \Re \left\{ [\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r})]^* \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\}. \end{aligned} \quad (3.63)$$

This is the general expression we get for the screening potential. We see that the screening potential is a functional of the total density and the orbitals just as promised in the beginning.

If we are calculating the ground-state¹ we know that the wavefunction is real, hence we get:

$$V_x^S(\mathbf{r}) = -\frac{1}{\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} [\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r})]^* \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (3.64)$$

3.3.2 KLI screening-response potential

Now we focus on the KLI screening-response potential, which was given as:

$$V_x^R(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \frac{\rho_{i\sigma}(\mathbf{r})}{2\rho(\mathbf{r})} \left[\langle v_x^{KLI} \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} \right] + c.c.. \quad (3.65)$$

Note that both the total density and single particle spin density are real, hence the only terms which could contain imaginary parts are $\langle v_x^{KLI} \rangle_{i\sigma}$ & $\langle u_{x,i\sigma} \rangle_{i\sigma}$. But since v_x^{KLI} is an actual potential we know that it must be real, and so must the spatial mean of the potential. This leaves the possibility that $\langle u_{x,i\sigma} \rangle_{i\sigma}$ could contain an imaginary part, but this term is shown to be real as well in appendix E. Hence we get:

$$V_x^R(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \frac{\rho_{i\sigma}(\mathbf{r})}{\rho(\mathbf{r})} \left[\langle v_x^{KLI} \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} \right]. \quad (3.66)$$

¹So far DFT can only be used to calculate the ground-state, but later we will introduce time-dependent density functional theory, which will allow us to calculate excited states as well.

Finally for closed shell systems we can remove the last term in the sum, since it can be shown that $\langle v_x^{KLI} \rangle_{N_\sigma\sigma} = \langle u_{x,i\sigma} \rangle_{N_\sigma\sigma}$ for closed shell systems. This is not a trivial thing to show, but a calculation of this can be found in [23]. When used we get:

$$\begin{aligned} V_x^R(\mathbf{r}) &= \sum_{\sigma} \sum_{i=1}^{N_\sigma-1} \frac{\rho_{i\sigma}(\mathbf{r})}{\rho(\mathbf{r})} \left[\langle v_x^{KLI} \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} \right] \\ &= \sum_{\sigma} \sum_{i=1}^{N_\sigma-1} \frac{\rho_{i\sigma}(\mathbf{r})}{\rho(\mathbf{r})} Q_{i\sigma}. \end{aligned} \quad (3.67)$$

So now the job is to find $Q_{i\sigma}$:

$$\begin{aligned} Q_{i\sigma} &= \langle v_x^{KLI} \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} \\ &= \langle V_x^S \rangle_{i\sigma} + \langle V_x^R \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma}. \end{aligned} \quad (3.68)$$

We focus on the spatial mean of the response function:

$$\langle V_x^R \rangle_{i\sigma} = \int d\mathbf{r} V_x^R(\mathbf{r}) |\varphi_{i\sigma}(\mathbf{r})|^2. \quad (3.69)$$

We insert the response functional as given in (3.67), and then we reorder the terms:

$$\begin{aligned} \langle V_x^R \rangle_{i\sigma} &= \int d\mathbf{r} \sum_{\sigma} \sum_{j=1}^{N_\sigma} \frac{\rho_{j\sigma}(\mathbf{r})}{\rho(\mathbf{r})} Q_{j\sigma} |\varphi_{i\sigma}(\mathbf{r})|^2 \\ &= \sum_{\sigma} \sum_{j=1}^{N_\sigma} Q_{j\sigma} \int d\mathbf{r} \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{\rho(\mathbf{r})} \\ &= \sum_{\sigma} \sum_{j=1}^{N_\sigma} Q_{j\sigma} M_{ji}. \end{aligned} \quad (3.70)$$

where M_{ji} is defined as:

$$M_{ji} = \int d\mathbf{r} \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{\rho(\mathbf{r})}. \quad (3.71)$$

By reordering (3.68) and inserting (3.70) into it, we get:

$$\begin{aligned} \langle V_x^S \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma} &= Q_{i\sigma} - \langle V_x^R \rangle_{i\sigma} \\ &= Q_{i\sigma} - \sum_{\sigma} \sum_{j=1}^{N_\sigma} Q_{j\sigma} M_{ji} \\ &= \sum_{\sigma} \sum_{j=1}^{N_\sigma} (\delta_{ij} - M_{ji}) Q_{j\sigma}. \end{aligned} \quad (3.72)$$

This is just a matrix equation, when reordered it might appear more clear:

$$\sum_{\sigma} \sum_{j=1}^{N_{\sigma}-1} (\delta_{ij} - M_{ji}) Q_{j\sigma} = \langle V_x^S \rangle_{i\sigma} - \langle u_{x,i\sigma} \rangle_{i\sigma}. \quad (3.73)$$

So now we need to find expressions for $\langle V_x^S \rangle_{i\sigma}$ and $\langle u_{x,i\sigma} \rangle_{i\sigma}$.

We start with $\langle u_{x,i\sigma} \rangle_{i\sigma}$.

$u_{x,i\sigma}$ is defined in (3.44) and by inserting (3.12) we get:

$$u_{x,i\sigma} = -\frac{1}{\varphi_{i\sigma}^*(\mathbf{r})} \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3.74)$$

its spatial mean is given in (3.55):

$$\begin{aligned} \langle u_{x,i\sigma} \rangle_{i\sigma} &= \int d\mathbf{r} \varphi_{i\sigma}^*(\mathbf{r}) u_{x,i\sigma}(\mathbf{r}) \varphi_{i\sigma}(\mathbf{r}) \\ &= -\int d\mathbf{r} \varphi_{i\sigma}(\mathbf{r}) \sum_{j=1}^{N_{\sigma}} \varphi_{j\sigma}^*(\mathbf{r}) \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (3.75)$$

Next we find $\langle V_x^S \rangle_{i\sigma}$.

V_x^S was calculated in (3.63), and its spatial mean is easily taken by using (3.53). Hence we get:

$$\begin{aligned} \langle V_x^S \rangle_{k\sigma} &= -\int d\mathbf{r} |\varphi_{k\sigma}(\mathbf{r})|^2 \frac{1}{\rho(\mathbf{r})} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \\ &\Re \left\{ [\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r})]^* \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right\}. \end{aligned} \quad (3.76)$$

Every term which is needed in order to calculate the KLI-potential has now been stated explicitly.

The KLI potential is the one we use in our numerical implementation, but before we can use it, we need to bring it all into the time-domain, this is done with the introduction of time-dependent density functional theory, which will be the main topic in the following chapter.

Chapter 4

Time-dependent quantum systems

We are now ready to move into the time-domain. Suppose we have a stationary system, but at some point in time we decide to put an external time-dependent potential on our system. We would expect the system to respond to the external potential, but so far we have no equation which can describe such a response.

The equation which we need in order to rectify this is called the time-dependent Schrödinger equation (TDSE)¹:

$$\frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{H}(t) \Psi(\mathbf{r}, t), \quad (4.1)$$

where $\hat{H}(t)$ is the time-dependent Hamiltonian and $\Psi(\mathbf{r}, t)$ is the time-dependent wavefunction.

The TDSE is a dynamical equation, which describes how a wavefunction evolves with time. From the TDSE one can derive the time-independent Schrödinger equation².

The TDSE can dynamically describe any quantum mechanical system, both the simple single free particle, and the complex surface dynamics of macroscopic objects. So the problem with the TDSE is not its range of validity, but rather that we are incapable of solving the equation for anything but the simplest systems, both analytically and numerically. The way to progress is as always by seeking new methods and making reasonable approximations where they are needed.

¹In the very first chapter of this thesis we mentioned that other formulations of quantum mechanics exists, this is also true in the time-domain, but since we started in the Schrödinger picture it is only natural to stay within that picture.

²This is done by splitting the wavefunction in a product of time and spatial dependence and assuming a time-independent Hamiltonian, for more detail see [24, p. 12].

What constitute a reasonable approximation depends upon the system of interest. In this thesis the systems of interest are, as previously mentioned, atoms and molecules. Just like in the time-independent case this leads us into the domain of many-body quantum systems.

So although the fundamental equation that describes our system has changed, the problem of many-body quantum systems, which was discussed in section 1.1, has not.

To avoid a complete repetition of the introduction in chapter 1, we will end this introduction by noting that the many-body problem is not made easier in the time-dependent domain, rather the contrary. Because of this a time-dependent density functional theory (TDDFT) was greatly sought.

4.1 Time-dependent density functional theory

After 1964, in which density functional theory (DFT) was first shown, many attempts to extend the theory to the time-domain were attempted. A few trys resulted in a TDDFT, but only for a very limited set of densities[25, 26, 27]. With an article in 1984[28], Runge-Gross (RG) were the first to extend the theory to a much more reasonable domain of densities, although later articles still uncovered some shortcomings in the RG theory[28]. Most of these shortcomings have later been fixed by various extendings[29, 28] to RG theory, much like Levy did for Hohenberg-Kohn's (HK) theory.

Lastly it should be noted that M. Ruggenthaler and R. van Leeuwen this year published a new TDDFT, which uses a different approach to the problem and further extend the domain of TDDFT theory[30]. This new theory is very focused on the underlying mathematics and may not be as intuitive. Because of this, the theory which will be presented in this thesis is the original TDDFT by Runge-Gross.

Theorem 4.1. (Runge-Gross theorem)

For every single-particle potential, $v(\mathbf{r}, t)$, which can be expanded into a Taylor series with respect to the time coordinate around $t = t_0$, a map $\check{G} : v(\mathbf{r}, t) \rightarrow \rho(\mathbf{r}, t)$ is defined by solving the time-dependent Schrödinger equation with a fixed initial state $\Psi(t_0) = \Psi_0$ and calculating the corresponding densities $\rho(\mathbf{r}, t)$. This map can be inverted up to an additive merely time-dependent function in the potential.

Hence the first RG theorem states that even in the time dependent case there exists a 1-1 correspondence between the external potential and the density. This is the time-dependent equivalent of HK's theorem, as given in section 1.2.1.

Proof. (Runge-Gross theorem)

Note that we use the formalism where ∇ only act on the first element to the right.

Let $v_1(\mathbf{r}, t)$ and $v_2(\mathbf{r}, t)$ be two external potentials which corresponds to the same wavefunction Ψ_0 at time t_0 , but in general differ by more than time-dependent function:

$$v_1(\mathbf{r}, t) - v_2(\mathbf{r}, t) \neq f(t). \quad (4.2)$$

We assume that the external potentials are Taylor expandable functions around $t = t_0$, which means that there exist some k such that:

$$\frac{\partial^k}{\partial t^k} [v_1(\mathbf{r}, t) - v_2(\mathbf{r}, t)]_{t=t_0} \neq \text{const.} \quad (4.3)$$

So the fact that we have chosen two potentials which at some point in time will differ, ensures that some order of derivative of the potentials will differ, even at the initial time.

Our final goal is to prove that the corresponding particle densities $\rho_1(\mathbf{r}, t)$ and $\rho_2(\mathbf{r}, t)$ are different. The way we do this is by first proving that the corresponding current densities $j_1(\mathbf{r}, t)$ and $j_2(\mathbf{r}, t)$ are different and through the continuity equation we then connect the current densities with the particle densities.

We know that the quantum mechanical current density operator $\hat{j}(\mathbf{r})$ is given as:

$$\hat{j}(\mathbf{r}) = \frac{1}{2i} \sum_{\sigma} \nabla \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) - \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \nabla \hat{\psi}_{\sigma}(\mathbf{r}), \quad (4.4)$$

with the current density related to the current density operator as:

$$j(\mathbf{r}, t) = \langle \Psi(t) | \hat{j}(\mathbf{r}) | \Psi(t) \rangle. \quad (4.5)$$

To connect the current density to the external potential we use Heisenbergs equation of motion:

$$i \frac{\partial}{\partial t} j(\mathbf{r}, t) = \langle \Psi(t) | [\hat{j}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle. \quad (4.6)$$

The difference between the two current densities is then:

$$\begin{aligned} i \frac{\partial}{\partial t} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)] &= \langle \Psi_1(t) | [\hat{j}(\mathbf{r}), \hat{H}_1(t)] | \Psi_1(t) \rangle \\ &\quad - \langle \Psi_2(t) | [\hat{j}(\mathbf{r}), \hat{H}_2(t)] | \Psi_2(t) \rangle. \end{aligned} \quad (4.7)$$

At the initial time t_0 we know that $\Psi_1(t_0) = \Psi_2(t_0) = \Psi_0$, hence we get:

$$i \frac{\partial}{\partial t} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]_{t=t_0} = \langle \Psi_0 | [\hat{j}(\mathbf{r}), \hat{H}_1(t_0) - \hat{H}_2(t_0)] | \Psi_0 \rangle. \quad (4.8)$$

By expanding the Hamiltonians in kinetic, external and internal functionals as done in (1.4), we can eliminate the kinetic and internal functional since these are the same for both Hamiltonians. We then get:

$$i \frac{\partial}{\partial t} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]_{t=t_0} = \langle \Psi_0 | [\hat{j}(\mathbf{r}), \hat{v}_1(t_0) - \hat{v}_2(t_0)] | \Psi_0 \rangle. \quad (4.9)$$

Now we need to evaluate the commutator. Calculating this commutator takes around 10 pages of calculation, so for the sake of clarity this is not done here, but can be found in appendix D. The result one gets for the commutator is given in equation (D.58), when inserted we get:

$$\frac{\partial}{\partial t} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]_{t=t_0} = -\rho(\mathbf{r}, t_0) \nabla_r [v_1(\mathbf{r}, t_0) - v_2(\mathbf{r}, t_0)]. \quad (4.10)$$

If k given in (4.3) is equal to zero. We can directly apply (4.3) which then gives us that the current densities will differ for $t > t_0$. If on the other hand $k > 0$, then we differentiate the above expression k times. This gives us:

$$\begin{aligned} \frac{\partial^{k+1}}{\partial t^{k+1}} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]_{t=t_0} &= -\frac{\partial^k}{\partial t^k} (\rho(\mathbf{r}, t))_{t=t_0} \nabla_r [v_1(\mathbf{r}, t_0) - v_2(\mathbf{r}, t_0)] \\ &\quad - \rho(\mathbf{r}, t_0) \nabla_r \frac{\partial^k}{\partial t^k} [v_1(\mathbf{r}, t) - v_2(\mathbf{r}, t)]_{t=t_0}. \end{aligned} \quad (4.11)$$

But since $k > 0$ we know from (4.3) that $v_1(\mathbf{r}, t_0) - v_2(\mathbf{r}, t_0) = \text{const}$, hence when we take the gradient of it in the first term it terminates:

$$\frac{\partial^{k+1}}{\partial t^{k+1}} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]_{t=t_0} = -\rho(\mathbf{r}, t_0) \nabla_r \frac{\partial^k}{\partial t^k} [v_1(\mathbf{r}, t) - v_2(\mathbf{r}, t)]_{t=t_0} \neq 0. \quad (4.12)$$

From this we can directly read that the current densities in general will differ for $t > t_0$.

This was the first part of the proof in which we showed that the difference in the external potential leads to a difference in the corresponding current densities.

Now we connect the difference in the current densities with a corresponding difference in the particle densities. Our starting point is the quantum mechanical continuity equation:

$$\frac{\partial}{\partial t} [\rho_1(\mathbf{r}, t) - \rho_2(\mathbf{r}, t)] = -\nabla \cdot [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]. \quad (4.13)$$

We take the $k + 1$ 'th time-derivative of the above and set $t = t_0$, which gives us:

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [\rho_1(\mathbf{r}, t) - \rho_2(\mathbf{r}, t)]_{t=t_0} = -\nabla \cdot \frac{\partial^{k+1}}{\partial t^{k+1}} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]_{t=t_0}. \quad (4.14)$$

We insert (4.12) on the right-hand side:

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [\rho_1(\mathbf{r}, t) - \rho_2(\mathbf{r}, t)]_{t=t_0} = \nabla \cdot \left\{ \rho(\mathbf{r}, t_0) \nabla_r \frac{\partial^k}{\partial t^k} [v_1(\mathbf{r}, t) - v_2(\mathbf{r}, t)]_{t=t_0} \right\}. \quad (4.15)$$

If we can show that the right hand side is in general not zero, we know that the particle densities on the left side will differ and the proof is done.

proof by *reductio ad absurdum*.

Assume that the right side is zero:

$$0 = \nabla \cdot [\rho(\mathbf{r}, t_0) \nabla u(\mathbf{r})], \quad (4.16)$$

where $u(\mathbf{r}) \neq \text{const}$, which we know from (4.3). We multiply the above by $u(\mathbf{r})$ and integrate the expression over all space:

$$0 = \int d\mathbf{r} u(\mathbf{r}) \nabla \cdot [\rho(\mathbf{r}, t_0) \nabla u(\mathbf{r})]. \quad (4.17)$$

By multiplying with $u(\mathbf{r})$ before we integrated, we can directly use the divergence theorem, which gives us:

$$0 = \int d\mathbf{r} \rho(\mathbf{r}, t_0) [\nabla u(\mathbf{r})]^2 + \oint d\mathbf{S} u(\mathbf{r}) \rho(\mathbf{r}, t_0) \nabla u(\mathbf{r}). \quad (4.18)$$

The last term can be rewritten using the fact that $\nabla(u^2) = 2u\nabla u$, which when inserted gives:

$$0 = \int d\mathbf{r} \rho(\mathbf{r}, t_0) [\nabla u(\mathbf{r})]^2 + \frac{1}{2} \oint d\mathbf{S} \rho(\mathbf{r}, t_0) \nabla [u(\mathbf{r})]^2. \quad (4.19)$$

Now we assume a finite density in space, hence by extending the surface integral to infinity we get zero contribution from that term¹. Hence we have:

$$0 = \int d\mathbf{r} \rho(\mathbf{r}, t_0) [\nabla u(\mathbf{r})]^2. \quad (4.20)$$

Since both terms are strictly positive the only way this can be true is if:

$$\rho(\mathbf{r}, t_0) [\nabla u(\mathbf{r})]^2 = 0. \quad (4.21)$$

Now we assume that the particle density does not exactly vanish at every point in space where $u(\mathbf{r})$ is not constant, then we have a contradiction. \square

¹At least for any realistic system which fall off at least as fast as $-1/r$.

4.1.1 Time-dependent Kohn-Sham equations

Now we know that in the time-domain, the potential is a functional of the density and the initial state. From here on it is a straightforward matter of extending the Kohn-Sham scheme to TDDFT¹. We define a fictitious system of noninteracting particles:

$$i\frac{\partial\varphi_{j\sigma}(\mathbf{r},t)}{\partial t} = \left[-\frac{\nabla^2}{2} + v_{KS}(\mathbf{r},t)\right]\varphi_{j\sigma}(\mathbf{r},t), \quad (4.22)$$

with the density given as:

$$\rho(\mathbf{r},t) = \sum_{\sigma} \sum_{j=1}^{N_{\sigma}} |\varphi_{j\sigma}(\mathbf{r},t)|^2. \quad (4.23)$$

The KS potential is defined such that the density match that of the real system. From TDDFT we know that such a potential exists and is unique - at least up to an irrelevant time-dependence. Just as in the time-independent case we split the KS-potential in several parts, which defines the xc-potential:

$$v_{KS}(\mathbf{r},t) = v_{ext}(\mathbf{r},t) + v_H(\mathbf{r},t) + v_{xc}(\mathbf{r},t), \quad (4.24)$$

where $v_{ext}(\mathbf{r},t)$ is the external potential, $v_H(\mathbf{r},t)$ is the Hartree potential as we know it from the time-independent case and finally $v_{xc}(\mathbf{r},t)$ is the now time-dependent xc-potential. The problem is however that this time-dependent xc-potential not only depends on the instantaneous particle density as it did in the time-independent case, but also on the entire history of the density and the initial wavefunctions.

A much more thorough investigation of why this happens and its consequences can be found in [28]. Here we just note that the dependence on the initial state can be dropped by only considering nondegenerate systems. The fact that the potential depends on the whole history of the density is removed by making the adiabatic approximation.

4.1.2 The adiabatic approximation

In the adiabatic approximation we assume a functional which is local in time. This is a good approximation for functionals which changes slowly. Because the system changes slowly compared to the electrons

¹Just to recap. The underlying idea behind Kohn-Sham is: Instead of calculating the dynamics of the complicated many-body system of interacting particles, we make a fictitious system of non-interacting particles moving in a now time-dependent effective Kohn-Sham potential, which is constructed in such a way that the density of the two systems are exactly the same.

we can assume that the system is always in its instantaneous ground-state. This allows us to directly use the functionals which we derived in the time-independent case:

$$v_{xc}^{adia}[\rho](\mathbf{r}, t) = V_{xc}^{GS}[\rho_{GS}](\mathbf{r})|_{\rho_{GS}(\mathbf{r}')=\rho(\mathbf{r}', t)}. \quad (4.25)$$

This was the end of the formal theory of DFT/TDDFT. In the rest of this thesis we will discuss our numerical implementation of TDDFT.

Chapter 5

Numerical implementation of TDDFT

With the formal theory of density functional theory (DFT) and time-dependent density functional theory (TDDFT) in place, it is time to move on to our numerical implementation of TDDFT.

Our numerical implementation of TDDFT uses the Kohn-Sham (KS) approach, in which we assume a nondegenerate ground state¹ and an adiabatic approximation². We ignore correlation effects and as our exchange functional we use the Optimised effective potential (OEP) with the KLI approximation as developed in section 3.1-3.3. The TDDFT solver is built on top of a single-active electron time dependent Schrödinger equation (SAE-TDSE) solver made by Thomas Kjeldsen[31]. The coding is done in Fortran 90/MPI. The system is simulated on an equidistant radial grid with an angular basis consisting of spherical harmonics.

The fact that we use a basis of spherical harmonics means that all the equations which we so far have derived will need to be converted to this basis, this is done in chapter 6.

In the following we illuminate the underlying TDSE solver and how we use it to solve the TDDFT problem.

5.1 Our TDDFT foundation

Before we go into greater detail about how the actual implementation of our TDDFT solver is done, we will shortly illuminate the underly-

¹By assuming nondegenerate ground states we can use DFT to make the ground state wavefunctions functionals of the density.

²The adiabatic approximation was shown in the last chapter to provide the link between TDDFT and DFT, hence by assuming the adiabatic approximation we can use the functionals and the theory we derived in DFT in the time domain.

ing central mechanics in the TDSE solver which our program is built on top of¹.

5.1.1 Our SAE-TDSE

As mentioned before the TDSE is in general too hard to solve, one way to fix this is through the SAE approximation. In the SAE approximation one assumes that any interesting dynamics only happens to one electron, usually the weakest bound. This active electron is assumed to move in a charge-sea made up all the other charged particles. Hence the SAE approximation turns the fully interacting Schrödinger equation into a non-interacting Schrödinger equation with an effective potential.

In order to progress the SAE-TDSE in time, the time-evolution operator approach is used².

Time evolution operator

The time evolution operator is the operator which fulfils:

$$\Psi(\mathbf{r}, t) = \hat{U}(t, t_0)\Psi(\mathbf{r}, t_0). \quad (5.1)$$

By use of the TDSE, the time evolution operator can be written as:

$$\hat{U}(t_2, t_1) = \hat{T} \exp \left(-i \int_{t_1}^{t_2} H(\tau) d\tau \right), \quad (5.2)$$

where \hat{T} denotes the time-ordering operator, which stems from the fact that a general Hamiltonian at time t does not commute with it self at time $t' \neq t$.

In order to progress further we make the time-steps sufficiently small. We can then assume that the Hamiltonian is constant in a given time-step, from this we get:

$$\hat{U}(t + \delta t, t) = \exp [-i\delta t H(\bar{t})], \quad (5.3)$$

where $\bar{t} = t + \delta t/2$.

The above is the foundation which we use to propagate the SAE-TDSE solver. The trick is now to figure out a numerical inexpensive way to apply this operator to the wavefunction. In order to apply the time evolution operator efficiently and in a numerical stable way, we can use several methods. Our SAE-TDSE program solves this problem by using the split operator approach, either in conjunction with a spectral algorithm or the Crank-Nicolson method.

¹A much more thorough presentation of the SAE-TDSE solver can be found in [31].

²For those unfamiliar with time-evolution operators, we recommend [32, p. 68].

Split operator approach

The split operator approach is, as the name implies, a method in which we split the operator in several parts. This in itself will not speed up the process but the idea is that it will be easier to optimize each term individually than the total Hamiltonian.

We set the expression up for the splitting by writing the Hamiltonian as a kinetic and potential part, when inserted into (5.3) we get:

$$\hat{U}(t + \delta t, t) = \exp [-i\delta t (\hat{T} + \hat{V}(\mathbf{r}, \bar{t}))]. \quad (5.4)$$

We wish to split this exponential into two kinds of exponentials, one containing the kinetic part and one containing the potential. In order to get a correct splitting to second order we split it the following way¹:

$$\hat{U}(t + \delta t, t) = e^{-i\delta t \hat{T}/2} e^{-i\delta t \hat{V}} e^{-i\delta t \hat{T}/2} + O(\delta t^3). \quad (5.5)$$

This was the split operator approach, now one can either apply the spectral algorithm or the Crank-Nicolson method.

Spectral algorithm

The potential operator \hat{V} is diagonal in coordinate space, hence taking the exponential of it wont be a problem². The kinetic operator on the other hand is a dense matrix in position space, but we know that it is diagonal in momentum space. The transformation between position and momentum space is the Fourier transform. So by applying the Fourier transform, before we apply the kinetic operator, we change to momentum space in which the kinetic operator is diagonal, and by applying the inverse Fourier transform afterwards we are able to return to position space again. This procedure is called the spectral algorithm, and all in all we have:

$$\begin{aligned} \Psi(\mathbf{r}, t + \delta t) = & F \cdot \text{diag} \left(e^{-i\frac{\delta t}{2} \hat{T}} \right) \cdot F^\dagger \cdot \text{diag} \left(e^{-i\delta t \hat{V}(\bar{t})} \right) \cdot F \cdot \text{diag} \left(e^{-i\frac{\delta t}{2} \hat{T}} \right) \\ & \cdot F^\dagger \cdot \Psi(\mathbf{r}, t) + O(\delta t^3), \end{aligned} \quad (5.6)$$

where F is the Fourier transformation, which is calculated using the Fast Fourier transformation algorithm.

Crank-Nicolson

Another way to calculate the time-evolution operator would be to make a Taylor expansion of the time evolution operator as given in

¹The error is due to the non commuting properties of \hat{T} and \hat{V} .

²The exponential of a diagonal matrix is nothing but the exponential of each individual entrance in the diagonal.

(5.3) and take the first order term. This method however turns out to be numerically unstable, mainly because of the asymmetric way in which this method evaluates the Hamiltonian operator¹. The modification that rectifies this problem is luckily quite simple, and with the modification the method is called the Crank-Nicolson method. The Crank-Nicolson method is both numerically stable and unitary, and it is given as:

$$\hat{U}_{CN}(t + \delta t, t) = \left(1 + \frac{1}{2}i\delta t\hat{H}(\bar{t})\right)^{-1} \cdot \left(1 - \frac{1}{2}i\delta t\hat{H}(\bar{t})\right). \quad (5.7)$$

By writing out the parenthesis one can see that we again have a correct splitting up to second order.

Note in the above we have applied the Crank-Nicolson method directly to the Hamiltonian, without using the split operator approach. This is one way to progress the equation, another way is to apply the Crank-Nicolson method after the split operator approach².

When combined with the split operator approach we get what is known as the modified Crank-Nicolson method, which turns out to be:

$$\begin{aligned} U(t + \delta t, t) &= e^{-i\delta t(\hat{T} + \hat{V})} \\ &\stackrel{CN}{=} \left(1 + i\frac{\delta t}{4}\hat{T}\right)^{-1} \left(1 - i\frac{\delta t}{4}\hat{T}\right) e^{-i\delta t\hat{V}} \left(1 + i\frac{\delta t}{4}\hat{T}\right)^{-1} \left(1 - i\frac{\delta t}{4}\hat{T}\right) \\ &+ O(\delta t^3). \end{aligned} \quad (5.8)$$

Caveat

The purpose of this section was to give a very compact introduction to the physics behind our SAE-TDSE program. The above constitute only the core skeletal structure of the program, it completely neglects a lot of finer details like the potentials block-diagonal structure or how the program is designed to be optimised for parallelization. For all these details see [31].

5.2 Converting SAE-TDSE to TDDFT

In the last section we showed how the SAE-TDSE solver works. Now note that the KS equations are nothing but a set of non-interacting TDSE, which is why we can use the TDSE solver as a foundation for a TDDFT simulator.

¹The assymetry is due to the fact that the Hamiltonian operator is only evaluated at the starting point of the interval with this method.

²We can freely apply it before or after because both routines are accurate to the same order.

Initially our idea was to build a TDDFT simulator as shown in figure 5.1. The neat thing about this idea is that everything is very clearly defined, each orbital has one computer node, there is no communication between these orbital nodes, instead they all communicate with a single master node, which at each timestep receives the output from the orbital nodes and use it to create the next KS potential and then sends this back.

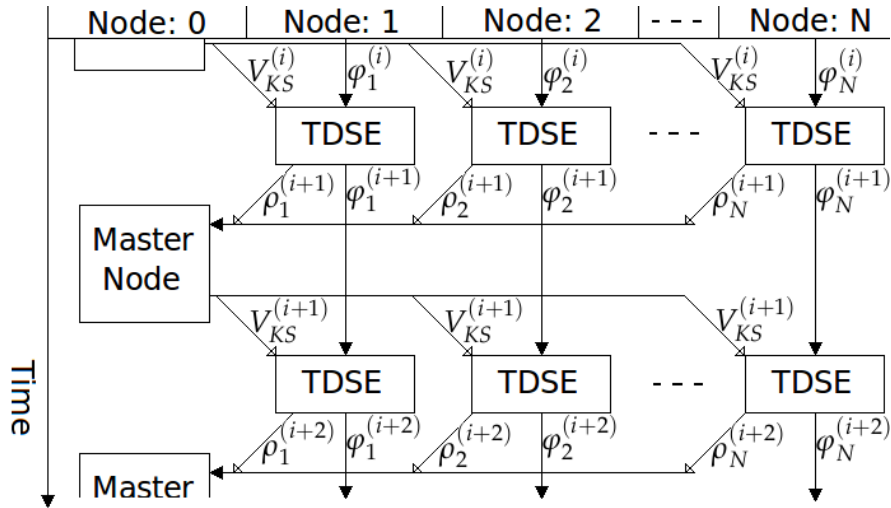


Figure 5.1: A simplified illustration of how the TDDFT solver can incorporate the SAE-TDSE solver. A timestep starts by giving the TDSE nodes the new KS potential and new orbitals. Each SAE-TDSE solver then evolves its orbital according to the new potential, when done they then send the corresponding density to the master node. The master node collect all the densities, and creates the next KS potential from it, which is then send back to all the SAE-TDSE nodes. And so continues the process.

While the master node calculates the new KS potential the TDSE nodes are idling which creates a bottleneck in the otherwise parallel system.

Note that spins have been ignored in the above for the sake of clarity.

Upon further inspection it turns out that there is a problem with this way of building a TDDFT solver. The problem is that while the actual TDSE calculation is completely parallel, the waiting time, while the master node calculates the new KS-potential is not at all parallel.

If the calculation of the KS potential is faster or at least comparable to one step through the TDSE solver, one could use the KS potential from the step before and thus remove the waiting. For small time-steps the KS potential should not change much¹, and hence this should be a good approximation which will remove the wait time. An illustration of this is shown in figure 5.2.

¹Remember we already have the adiabatic approximation which assumes this.

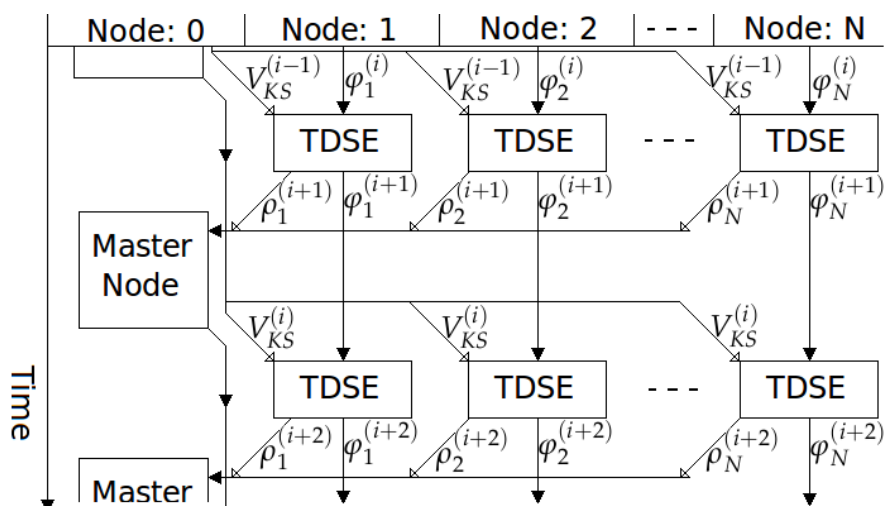


Figure 5.2: A bit more complex illustration of how the TDDFT solver can incorporate the SAE-TDSE solver. the i 'th timestep starts by giving the TDSE nodes the $i - 1$ 'th KS-potential and the i 'th orbitals. Each SAE-TDSE solver then evolves its orbital according to the potential, when done they then send the corresponding density to the master node. The master node collect all the densities, while sending the i 'th KS potential back to the nodes, which it has calculated while the TDSE nodes was working.

This method can turn the system completely parallel provided that the master node can calculate the KS-potential faster than the TDSE nodes can propagate a timestep.

Note that spins have been ignored in the above for the sake of clarity.

If the calculation of the KS potential goes much slower than one step through the TDSE solver the issue becomes much more problematic. In that case one either have to accept some wait time or use a much outdated KS potential.

In our case we use a very complicated xc-potential, hence the calculation of the KS potential takes a long time compared to a single step in the TDSE solver. For now we would not benefit much from having having a master node to calculate the KS potential¹. Instead every node does it own calculation of the potential, this of course means much more overall data-transfer, but the amount of overall data transfer is not that important. The important parameter is that the amount of data each node receives is not much different from the amount of data the master node receives in the cases shown in figure 5.1 & 5.2. By doing the parallelization this way we can use one less node.

¹This could however become relevant again once the solver is completed and optimization has been done.

But before any of this becomes relevant we require a way to find the initial orbitals, which we need to propagate a system. There are several ways to calculate the initial orbitals. Initially we considered direct diagonalization. Direct diagonalization turned out to be impractical due to several issues, first of all it was incompatible with the split operator approach which we incorporate, so an implementation would require a major overhaul of the TDSE code. Second, the size of the matrix that we would need to diagonalize would be very big, which would make this approach in the very least a daunting task, if not downright impossible.

Instead we settled on imaginary time propagation (ITP), which can be naturally incorporated with little effort.

5.3 Imaginary time propagation

We know that the eigenstates, $\varphi_i(\mathbf{r})$, of any system form a complete set, hence any random wavefunction, $\psi(\mathbf{r}, t)$, can be represented in this basis:

$$\psi(\mathbf{r}, t) = \sum_i c_i(t) \varphi_i(\mathbf{r}). \quad (5.9)$$

We also know that the propagation of a wavefunction can be done by the infinitesimal time evolution operator as given in (5.3):

$$\psi(\mathbf{r}, t + \delta t) = e^{-i\delta t H} \psi(\mathbf{r}, t) + O(\delta t^3). \quad (5.10)$$

By making the shift into the imaginary plane, $t \rightarrow -it$, we get:

$$\psi(\mathbf{r}, -i(t + \delta t)) = e^{-\delta t H} \psi(\mathbf{r}, -it) + O(\delta t^3). \quad (5.11)$$

So we see that the shift triggers an exponential decay of the wavefunctions. By inserting the eigenstates the weight of the exponential decay becomes clear:

$$\psi(\mathbf{r}, t + \delta t) = \sum_i c_i(t) \varphi_i(\mathbf{r}) e^{-E_i \delta t} + O(\delta t^3), \quad (5.12)$$

hence the decay of each eigenstate depends upon its eigenvalue. The ground state is the one with the lowest eigenvalue and hence it decays the slowest. So by keep applying the imaginary time propagator we will introduce an exponential decay in all the eigenstates, but because the ground state has the lowest energy it will decay the slowest. Due to numerical stability and to check convergence one should renormalise the system after each ITP. In the end the above method will converge, and the trial wavefunction will in practice be identical to the ground state wavefunction.

For any propagation simulator this method is a natural way to receive the ground state, but it is also suitable to find other low energy states. In order to find the second lowest energy state of a system, one has to use a second trial wavefunction. After each ITP one orthogonalises the second trial function on the first and thus remove any small trace the second trial function might have of the first. Eventually the first trial function will converge to the ground state, whereas the second will converge to the second lowest state.

Several routines exists to orthogonalise a set of functions. In our code we use subspace orthogonalisation, because this method of converging is claimed to be faster[33]. Subspace orthogonalisation will be discussed on page 59.

The above procedure is how we find our initial orbitals and the ITP is repeated until convergence is reached¹.

¹Checking convergence can be done in a lot of ways, the simplest is to check whether the eigenenergies of the system are converged. More sophisticated criteria can be found in [33].

Caveat

Normally in ITP one uses a static potential and hence one knows that the routine is stable.

In our case however our potential depends on the density. It is not clear to us if this is a stable process, and whether or not the initial state of the trial orbitals have any influence upon the final configuration. (One could easily imagine that the random potential due to the random orbitals will lead to a stable but wrong final state.)

We have tried several ways to test this, first and foremost we have tried running the program multiple times and see if we get consistent results even though the initial state is random. So far it appears stable.

Secondly we have limited the starting trial orbitals to only contain amplitude of the angular momentums they could contain, to see if this made a difference. Again it does not appear to make a difference.

Finally we tried to start out with only the static potentials on and then slowly turn on the different dynamic potentials. Again it appears to be stable.

Nevertheless this is still a concern to us, until proven otherwise.

Subspace orthogonalisation

Instead of the usual Gram-Schmidt or modified Gram-Schmidt orthogonalisation, we use subspace orthogonalisation as recommended in [33].

We calculate the overlap matrix

$$M_{ij} = \langle \varphi_i^{(k+1)} | \varphi_j^{(k+1)} \rangle, \quad (5.13)$$

and solve the eigenvalue problem,

$$\sum_j M_{ij} c_j^{(n)} = m_n c_i^{(n)}. \quad (5.14)$$

From this the new trial functions are created:

$$| \psi_j^{(k+1)} \rangle = \frac{1}{\sqrt{m_j}} \sum_i c_i^{(j)} | \varphi_i^{(k+1)} \rangle. \quad (5.15)$$

Finally we get the normalisation energies from the eigenvalues:

$$m_j^{(k)} = \exp \left(-2\delta t E_j^{(k)}(\delta t) \right) \rightarrow m_j = \exp \left(-2\delta t E_j(\delta t) \right). \quad (5.16)$$

Imaginary time propagation - Advanced

At one point we investigated a method to speed up the convergence of ITP. The idea was to raise the order of accuracy of the ITP by using

a more complicated propagation operator[33, 34]:

$$e^{-\delta t(\hat{T}+\hat{V})} = \sum_{k=1}^n c_k T_2^k \left(\frac{\delta t}{k} \right) + O(\delta t^{2n+1}). \quad (5.17)$$

with

$$T_2 \left(\frac{\delta t}{k} \right) = e^{-1/2\delta t\hat{V}} e^{-\delta t\hat{T}} e^{-1/2\delta t\hat{V}} \quad (5.18)$$

and the coefficient given as:

$$c_i = \prod_{j \neq i}^n \frac{i^2}{i^2 - j^2} \quad (5.19)$$

This can reduce the number of Fourier transforms required in an ITP. The problem with this method, is that one propagation step will be much longer and we will not be able to update our KS potential until after the full step. Hence this method might be superior for static potentials, but it is not for self correcting potentials like ours.

Another advanced ITP method which we looked at was varying the size of the time-steps. The idea was in simple terms to regulate it by creating an inner and outer accuracy. Whenever the inner accuracy reached a certain value, the outer accuracy would be checked, and if it was not also at the desired value, the size of the timesteps would be doubled and the propagation would run again until the inner accuracy would get sufficiently low again. This method is described in [33], along with the possibility of parallelisation. In the end, this method was not employed since it showed no upgrade in speed for our program, compared to the simple method.

Chapter 6

Conversion to reduced spherical harmonics

In this section we look at all the relevant part of the general theory. We expand these parts and convert the orbitals to reduced orbitals, and expand those in a spherical harmonic basis, this combined process we refer to as reduced spherical harmonics.

6.1 Reduced orbitals

The relation between an orbital $\varphi_{i\sigma}$ and its reduced counterpart $\tilde{\zeta}_{i\sigma}$ is given as:

$$\tilde{\zeta}_{i\sigma}(r, \Omega, t) = r\varphi_{i\sigma}(r, \Omega, t), \quad (6.1)$$

where Ω is the angular dependence, $\Omega = (\theta, \varphi)$.

We introduce the reduced orbital because it is convenient. We know that the reduced orbital is 0 in origo, unless the original orbital is divergent in origo. Hence we get the much needed and very simple boundary condition:

$$\tilde{\zeta}_{i\sigma}(0, \Omega, t) = 0. \quad (6.2)$$

6.2 Spherical Harmonic basis

Spherical harmonics are the natural basis to work in when working with atomic and molecular systems. Each spherical harmonic corresponds to a different orbital, hence the spherical harmonics have a direct physical interpretation, and because of this physical interpretation we also know that many system can be described accurately with a relatively small set of spherical harmonics.

The problem with working in spherical harmonics is however that we need to convert anything we want to use or calculate to the basis first. This is done in the rest of this chapter¹.

For those unfamiliar with spherical harmonics, see appendix A which contains some of the more frequently used spherical harmonic relations.

Because the spherical harmonics form a complete set in Hilbert space, anything can be expressed in it. So given a function, $X(\mathbf{r}, t)$, it can be expressed as:

$$X(\mathbf{r}, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l X_{lm}(r, t) Y_{lm}(\Omega). \quad (6.3)$$

We choose to expand the reduced orbital in spherical harmonics:

$$\zeta_{i\sigma}(\mathbf{r}, t) = \sum_{l=0}^{l_{max}} \sum_{m=-l}^l f_{lm,i\sigma}(r, t) Y_{lm}(\Omega), \quad (6.4)$$

note that we choose a maximum angular momentum quantum number and cut off anything higher than this. To keep things consistent, this means that the original orbital is given as:

$$\varphi_{i\sigma}(\mathbf{r}, t) = \frac{1}{r} \sum_{l=0}^{l_{max}} \sum_{m=-l}^l f_{lm,i\sigma}(r, t) Y_{lm}(\Omega). \quad (6.5)$$

¹It should be noted that **Dieter Bauer** has made a similar conversion to spherical harmonics, but differences in definitions and methods makes comparison difficult[35, 36].

6.3 The density, $\rho(\mathbf{r}, t)$

We calculate the density, which is central in computing the direct- and exchange-potential.

The density is related to the orbital in the following way:

$$\rho(\mathbf{r}, t) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\varphi_{i\sigma}(\mathbf{r}, t)|^2. \quad (6.6)$$

In the following we calculate the more general term $\varphi_{i\sigma}^*(\mathbf{r}, t)\varphi_{j\sigma}(\mathbf{r}, t)$ which will be used many times. By inserting (6.5) the orbitals are converted to the reduced spherical harmonics:

$$\begin{aligned} \varphi_{i\sigma}^*(\mathbf{r}, t)\varphi_{j\sigma}(\mathbf{r}, t) &= \frac{1}{r^2} \left[\sum_{l=0}^{l_{max}} \sum_{m=-l}^l f_{lm,i\sigma}(r, t) Y_{lm}(\Omega) \right] \\ &\quad \left[\sum_{l'=0}^{l'_{max}} \sum_{m'=-l'}^{l'} f_{l'm',i\sigma}(r, t) Y_{l'm'}(\Omega) \right]^* \\ &= \frac{1}{r^2} \sum_{lm, l'm'} f_{l'm',i\sigma}^*(r, t) f_{lm,j\sigma}(r, t) Y_{l'm'}^*(\Omega) Y_{lm}(\Omega), \end{aligned} \quad (6.7)$$

We convert the spherical harmonic to its complex conjugate:

$$\varphi_{i\sigma}^*(\mathbf{r}, t)\varphi_{j\sigma}(\mathbf{r}, t) = \frac{1}{r^2} \sum_{lm, l'm'} (-1)^{m'} f_{l'm',i\sigma}^*(r, t) f_{lm,j\sigma}(r, t) Y_{l'-m'}(\Omega) Y_{lm}(\Omega). \quad (6.8)$$

A product of spherical harmonics can be calculated using Clebsch-Gordan (CG) coefficients, the relation is given in (A.6):

$$\begin{aligned} Y_{l_1 m_1}(\Omega) Y_{l_2 m_2}(\theta, \varphi) &= \sum_{l=|l_1-l_2|}^{l_1+l_2} \sum_{m=-l}^l \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}} \\ &\quad C_{l_1 0 l_2 0}^{l 0} C_{l_1 m_1 l_2 m_2}^{l m} Y_{lm}(\Omega). \end{aligned} \quad (A.6)$$

By using the above relation we get:

$$\begin{aligned} \varphi_{i\sigma}^*(\mathbf{r}, t)\varphi_{j\sigma}(\mathbf{r}, t) &= \frac{1}{r^2} \sum_{lm, l'm'} (-1)^{m'} f_{l'm',i\sigma}^*(r, t) f_{lm,j\sigma}(r, t) \sum_{L=|l-l'|}^{\min\{|l+l'|, l_{max}\}} \\ &\quad \sum_{M=-L}^L \sqrt{\frac{(2l+1)(2l'+1)}{4\pi(2L+1)}} C_{l 0 l' 0}^{L 0} C_{l m l' -m'}^{L M} Y_{LM}(\Omega) \\ &= \frac{1}{\sqrt{4\pi} r^2} \sum_{lm, l'm', LM} (-1)^{m'} \sqrt{\frac{(2l+1)(2l'+1)}{2L+1}} \\ &\quad C_{l 0 l' 0}^{L 0} C_{l m l' -m'}^{L M} f_{l'm',i\sigma}^*(r, t) f_{lm,j\sigma}(r, t) Y_{LM}(\Omega), \end{aligned} \quad (6.9)$$

note that the sum over L is still restricted to a maximum of l_{max} . Finally we write the expression out in its full length again and change the summation order:

$$\begin{aligned}
\varphi_{i\sigma}^*(\mathbf{r}, t)\varphi_{j\sigma}(\mathbf{r}, t) &= \frac{1}{\sqrt{4\pi}r^2} \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \sum_{l'=0}^{l_{max}} \sum_{m'=-l'}^{l'} \sum_{L=|l-l'|}^{\min\{|l+l'|, l_{max}\}} \sum_{M=-L}^L \\
&\quad (-1)^{m'} \sqrt{\frac{(2l+1)(2l'+1)}{2L+1}} C_{l0l'0}^{L0} C_{lm'l'-m'}^{LM} \\
&\quad f_{l'm',i\sigma}^*(r, t) f_{lm,j\sigma}(r, t) Y_{LM}(\Omega) \\
&= \frac{1}{\sqrt{4\pi}r^2} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \sum_{l'=|L-l|}^{\min\{|L+l|, l_{max}\}} \sum_{m'=-l'}^{l'} \\
&\quad (-1)^{m'} \sqrt{\frac{(2l+1)(2l'+1)}{2L+1}} C_{l0l'0}^{L0} C_{lm'l'-m'}^{LM} \\
&\quad f_{l'm',i\sigma}^*(r, t) f_{lm,j\sigma}(r, t) Y_{LM}(\Omega).
\end{aligned} \tag{6.10}$$

We know that CG coefficients fulfil the following relation¹:

$$C_{l0l'0}^{L0} C_{lm'l'-m'}^{LM} = \frac{2L+1}{2l'+1} C_{l0L0}^{l'0} C_{lmLM}^{l'm'} \tag{6.11}$$

By using the above relation we get:

$$\begin{aligned}
\varphi_{i\sigma}^*(\mathbf{r}, t)\varphi_{j\sigma}(\mathbf{r}, t) &= \frac{1}{\sqrt{4\pi}r^2} \sum_{LM, lm, l'm'} (-1)^{m'} \sqrt{(2L+1) \frac{2l+1}{2l'+1}} \\
&\quad C_{l0L0}^{l'0} C_{lmLM}^{l'-m'} f_{l'm',i\sigma}^*(r, t) f_{lm,j\sigma}(r, t) Y_{LM}(\Omega).
\end{aligned} \tag{6.12}$$

Finally we define the function $\Lambda_{ji}^{LM}(r, t)$:

$$\begin{aligned}
\Lambda_{ji}^{LM}(r, t) &= \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \sum_{l'=|L-l|}^{\min\{|L+l|, l_{max}\}} \sum_{m'=-l'}^{l'} (-1)^{m'} \\
&\quad \sqrt{\frac{(2l+1)}{(2l'+1)}} C_{l0L0}^{l'0} C_{lmLM}^{l'-m'} f_{lm,j\sigma}(r, t) f_{l'm',i\sigma}^*(r, t).
\end{aligned} \tag{6.13}$$

$\Lambda_{ji}^{LM}(r, t)$ is calculated in our program. This enables us to write the desired expression in a much shorter form:

$$\varphi_{i\sigma}^*(\mathbf{r}, t)\varphi_{j\sigma}(\mathbf{r}, t) = \frac{1}{\sqrt{4\pi}r^2} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ji}^{LM}(r, t) Y_{LM}(\Omega). \tag{6.14}$$

¹For people not comfortable with CG coefficients see [37].

Now we are finally ready to calculate the density. We insert (6.14) with $i = j$ into (6.6):

$$\begin{aligned}
 \rho(\mathbf{r}, t) &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} |\varphi_{i\sigma}(\mathbf{r}, t)|^2 \\
 &= \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \frac{1}{\sqrt{4\pi r^2}} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ii}^{LM}(r, t) Y_{LM}(\Omega) \quad (6.15) \\
 &= \frac{1}{\sqrt{4\pi r^2}} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ii}^{LM}(r, t) Y_{LM}(\Omega).
 \end{aligned}$$

This is how we calculate the density, $\rho(\mathbf{r}, t)$ in the program.

6.4 The Hartree potential, $V_H(\mathbf{r}, t)$

With the density calculated, we now do the calculation of the Hartree potential.

The Hartree potential is given in (1.49):

$$V_H(\mathbf{r}, t) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (6.16)$$

The density is calculated and stored in our code, hence we got $\rho(\mathbf{r}, t)$ on the form:

$$\rho(\mathbf{r}', t) = \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \rho_{LM}(r', t) Y_{LM}(\Omega'). \quad (6.17)$$

To deal with the denominator of (6.16), we use (A.7):

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{(r_{<})^l}{(r_{>})^{l+1}} Y_{lm}^*(\Omega) Y_{lm}(\Omega'), \quad (A.7)$$

note the symmetry between \mathbf{r} & \mathbf{r}' . With (6.17) & (A.7) given, we calculate (6.16).

By insertion we get:

$$\begin{aligned} V_H(\mathbf{r}, t) &= \int d\mathbf{r}' \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \rho_{LM}(r', t) Y_{LM}(\Omega') \\ &\quad \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{(r_{<})^l}{(r_{>})^{l+1}} Y_{lm}^*(\Omega') Y_{lm}(\Omega) \\ &= \sum_{LM, lm} \frac{4\pi}{2l+1} \int d\mathbf{r}' \rho_{LM}(r', t) \frac{(r_{<})^l}{(r_{>})^{l+1}} Y_{LM}(\Omega') Y_{lm}^*(\Omega') Y_{lm}(\Omega). \end{aligned} \quad (6.18)$$

Next the integral is split in radial and angular part:

$$\begin{aligned} V_H(\mathbf{r}, t) &= \sum_{LM, lm} \frac{4\pi}{2l+1} \int dr' \rho_{LM}(r', t) \frac{(r_{<})^l}{(r_{>})^{l+1}} \\ &\quad \int d\Omega' Y_{LM}(\Omega') Y_{lm}^*(\Omega') Y_{lm}(\Omega). \end{aligned} \quad (6.19)$$

To evaluate the angular integral we can use (A.5):

$$\int Y_{l_1 m_1}^*(\Omega) Y_{l_2 m_2}(\Omega) d\Omega = \delta_{l_1, l_2} \delta_{m_1, m_2}. \quad (A.5)$$

By using the above relation we get:

$$\begin{aligned}
 V_H(\mathbf{r}, t) &= \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \frac{4\pi}{2l+1} \\
 &\int dr' \left[r'^2 \rho_{LM}(r', t) \frac{(r_{<})^l}{(r_{>})^{l+1}} \right] \delta_{Ll} \delta_{Mm} Y_{lm}(\Omega) \quad (6.20) \\
 &= \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \frac{4\pi}{2l+1} \int dr' \left[r'^2 \rho_{lm}(r', t) \frac{(r_{<})^l}{(r_{>})^{l+1}} \right] Y_{lm}(\Omega).
 \end{aligned}$$

The radial integral is one we will encounter several times doing the following calculations, because of this we will not solve it here. Instead it is solved more generally in appendix B.

6.5 The spin-dependent exchange potential,

$$V_{x,\sigma}^{KLI}(\mathbf{r}, t)$$

We use the optimised effective potential (OEP), with the KLI-approximation as developed in section 3.1-3.3. The KLI potential was in (3.59) split in two terms:

$$v_x^{KLI}(\mathbf{r}, t) = V_x^S(\mathbf{r}, t) + V_x^R(\mathbf{r}, t), \quad (6.21)$$

where $V_x^S(\mathbf{r}, t)$ is known as the screening potential, and $V_x^R(\mathbf{r}, t)$ is known as the screening-response potential, as noted in section 6.5.

Since each orbital only reacts to a part of the total potential, namely the part created from equal spin particles it makes better sense to split the potential into the different spins:

$$\begin{aligned} v_x^{KLI}(\mathbf{r}, t) &= \sum_{\sigma} v_{x,\sigma}^{KLI}(\mathbf{r}, t) \\ &= \sum_{\sigma} \left[V_{x,\sigma}^S(\mathbf{r}, t) + V_{x,\sigma}^R(\mathbf{r}, t) \right]. \end{aligned} \quad (6.22)$$

The two spin dependent potentials are evaluated in the following.

6.5.1 Spin-dependent screening potential, $V_x^S(\mathbf{r}, t)$

We calculate an expression for the spin-dependent screening potential.

In (3.63) we found the following expression for the screening potential:

$$\begin{aligned} V_x^S(\mathbf{r}, t) &= -\frac{1}{\rho(\mathbf{r}, t)} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \Re \left\{ [\varphi_{i\sigma}^*(\mathbf{r}, t) \varphi_{j\sigma}(\mathbf{r}, t)]^* \right. \\ &\quad \left. \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}', t) \varphi_{j\sigma}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \right\}. \end{aligned} \quad (3.63)$$

So the spin-dependent potential which we want is given as:

$$\begin{aligned} V_{x,\sigma}^S(\mathbf{r}, t) &= -\frac{1}{\rho_{\sigma}(\mathbf{r}, t)} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \Re \left\{ [\varphi_{i\sigma}^*(\mathbf{r}, t) \varphi_{j\sigma}(\mathbf{r}, t)]^* \right. \\ &\quad \left. \int d\mathbf{r}' \frac{\varphi_{i\sigma}^*(\mathbf{r}', t) \varphi_{j\sigma}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \right\}. \end{aligned} \quad (6.23)$$

Evaluating this gets much simpler if use what we have previously derived.

In (6.14) & (A.7) we have:

$$\varphi_{i\sigma}^*(\mathbf{r}, t) \varphi_{j\sigma}(\mathbf{r}, t) = \frac{1}{\sqrt{4\pi r^2}} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ji}^{LM}(r, t) Y_{LM}(\Omega), \quad (6.14)$$

and

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{(r_{<})^l}{(r_{>})^{l+1}} Y_{lm}^*(\Omega) Y_{lm}(\Omega'). \quad (\text{A.7})$$

By combining the above expression we are able to find an expression for the integral in (3.63):

$$\begin{aligned} \int d^3r' \frac{\varphi_{i\sigma}^*(\mathbf{r}', t) \varphi_{j\sigma}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} &= \int d^3r' \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}(\Omega) Y_{lm}^*(\Omega') \\ &\quad \frac{1}{\sqrt{4\pi} r'^2} \sum_{L=0}^L \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ji}^{LM}(r', t) Y_{LM}(\Omega') \\ &= \sqrt{4\pi} \sum_{lm, LM} \frac{\sqrt{2L+1}}{2l+1} \int d^3r' \frac{1}{r'^2} \frac{r_{<}^l}{r_{>}^{l+1}} \Lambda_{ji}^{LM}(r', t) \\ &\quad Y_{lm}(\Omega) Y_{lm}^*(\Omega') Y_{LM}(\Omega'). \end{aligned} \quad (\text{6.24})$$

The integral is split into radial and angular part:

$$\begin{aligned} \int d^3r' \frac{\varphi_{i\sigma}^*(\mathbf{r}', t) \varphi_{j\sigma}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} &= \sqrt{4\pi} \sum_{lm, LM} \frac{\sqrt{2L+1}}{2l+1} \int dr' \frac{r_{<}^l}{r_{>}^{l+1}} \Lambda_{ji}^{LM}(r', t) \\ &\quad Y_{lm}(\Omega) \int d\Omega' Y_{lm}^*(\Omega') Y_{LM}(\Omega'). \end{aligned} \quad (\text{6.25})$$

The angular integral is solved using (A.5):

$$\begin{aligned} \int d^3r' \frac{\varphi_{i\sigma}^*(\mathbf{r}', t) \varphi_{j\sigma}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} &= \sqrt{4\pi} \sum_{lm} \sum_{LM} \frac{\sqrt{2L+1}}{2l+1} \\ &\quad \int dr' \frac{r_{<}^l}{r_{>}^{l+1}} \Lambda_{ji}^{LM}(r', t) Y_{lm}(\Omega) \delta_{lL} \delta_{mM} \\ &= \sqrt{4\pi} \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l \frac{1}{\sqrt{2l+1}} \\ &\quad \int dr' \frac{r_{<}^l}{r_{>}^{l+1}} \Lambda_{ji}^{lm}(r', t) Y_{lm}(\Omega). \end{aligned} \quad (\text{6.26})$$

The spin-dependent screening potential is calculated by inserting

(6.26) & (6.14) into (6.23):

$$\begin{aligned}
V_{x,\sigma}^S(\mathbf{r}, t) &= -\frac{1}{\rho_\sigma(\mathbf{r}, t)} \sum_{ij} \Re \left\{ \left[\frac{1}{\sqrt{4\pi r^2}} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ji}^{LM}(r, t) Y_{LM}(\Omega) \right]^* \right. \\
&\quad \left. \sqrt{4\pi} \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \frac{1}{\sqrt{2l+1}} \int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t) Y_{lm}(\Omega) \right\} \\
&= -\frac{1}{r^2 \rho_\sigma(\mathbf{r}, t)} \sum_{ij} \sum_{lm, LM} \sqrt{\frac{2L+1}{2l+1}} \\
&\quad \Re \left\{ \Lambda_{ji}^{LM*}(r, t) Y_{LM}^*(\Omega) \int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t) Y_{lm}(\Omega) \right\}.
\end{aligned} \tag{6.27}$$

The relation between a spherical harmonic and its complex conjugate as given in (A.4) is used:

$$\begin{aligned}
V_{x,\sigma}^S(\mathbf{r}, t) &= -\frac{1}{r^2 \rho_\sigma(\mathbf{r}, t)} \sum_{ij} \sum_{lm, LM} (-1)^M \sqrt{\frac{2L+1}{2l+1}} \\
&\quad \Re \left\{ \Lambda_{ji}^{LM*}(r, t) \int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t) Y_{L-M}(\Omega) Y_{lm}(\Omega) \right\}.
\end{aligned} \tag{6.28}$$

The product of spherical harmonics is given in (A.6), when used we get:

$$\begin{aligned}
V_{x,\sigma}^S(\mathbf{r}, t) &= -\frac{1}{r^2 \rho_\sigma(\mathbf{r}, t)} \sum_{ij} \sum_{lm, LM} (-1)^M \sqrt{\frac{2L+1}{2l+1}} \\
&\quad \Re \left\{ \Lambda_{ji}^{LM*}(r, t) \int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t) \sum_{l'=|L-l|}^{\min\{l_{max}, |L+l|\}} \sum_{m'=-l'}^{l'} \right. \\
&\quad \left. \sqrt{\frac{(2L+1)(2l+1)}{4\pi(2l'+1)}} C_{l0l0}^{l'0} C_{lmL-M}^{l'm'} Y_{l'm'}(\Omega) \right\}.
\end{aligned} \tag{6.29}$$

After some rearranging we get:

$$\begin{aligned}
V_{x,\sigma}^S(\mathbf{r}, t) &= -\frac{1}{\sqrt{4\pi r^2} \rho_\sigma(\mathbf{r}, t)} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sum_{l'=|L-l|}^{\min\{l_{max}, |L+l|\}} \\
&\quad \sum_{m'=-l'}^{l'} (-1)^M \frac{2L+1}{\sqrt{2l'+1}} \\
&\quad \Re \left\{ \Lambda_{ji}^{LM*}(r, t) \int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t) C_{l0l0}^{l'0} C_{lmL-M}^{l'm'} Y_{l'm'}(\Omega) \right\}.
\end{aligned} \tag{6.30}$$

So far everything is exact, we will now make various approximations to make this numerically easier to calculate. If we only consider ground states we know that the corresponding wavefunction is real. In similar spirit we make the approximation that all our orbitals are real. By using this we then get:

$$V_{x,GS,\sigma}^S(\mathbf{r}, t) = -\frac{1}{\sqrt{4\pi r^2} \rho_\sigma(\mathbf{r}, t)} \sum_{ij} \sum_{lm, LM, l'm'} (-1)^M \frac{2L+1}{\sqrt{2l'+1}} \Lambda_{ji}^{LM}(r, t) \int dr' \frac{r'^l}{r^{l+1}} \Lambda_{ji}^{lm}(r', t) C_{l0l0}^{l'0} C_{lmL-M}^{l'm'} Y_{l'm'}(\Omega). \quad (6.31)$$

Next we assume that each orbital only contain one m value¹, by using this assumption the ground state screening potential reduces even further:

$$V_{x,GS,\sigma}^S(\mathbf{r}, t) = -\frac{1}{\sqrt{4\pi r^2} \rho_\sigma(\mathbf{r})} \sum_{ij} \sum_{l,L,l'} (-1)^{-m_i-m_j} \frac{2L+1}{\sqrt{2l'+1}} \Lambda_{ji}^{L-m_i-m_j}(r, t) \int dr' \frac{r'^l}{r^{l+1}} \Lambda_{ji}^{l-m_i-m_j}(r', t) C_{l0l0}^{l'0} C_{l-m_i-m_j, Lm_i+m_j}^{l'0} Y_{l'0}(\Omega), \quad (6.32)$$

here we used the fact that Λ_{ji}^{LM*} contains a CG coefficient, which gives the constraint $M = -m_j - m_i$. Similarly the CG coefficient in Λ_{ji}^{lm} gives us $m = -m_j - m_i$, hence $m = M$. Finally if we use these restraints on our CG-coefficient $C_{lmL-M}^{l'm'}$ we get that $m' = 0$.

Unfortunately we are not done with the approximations just yet, we still need to do something about the inverse spin-density. We could expand the inverse spin-density as a Taylor series and then couple the resulting products of spherical harmonics, but such a process turns out to be both expensive and inaccurate².

Instead we make the assumption that all terms with $l > 0$ is neglected³. So we only take the angular independent term of our $\rho_\sigma(\mathbf{r}, t)$ expansion as given in (6.17), when inserted we get:

$$V_{x,GS,\sigma}^S(\mathbf{r}, t) = -\frac{1}{\sqrt{4\pi r^2} \rho_{00,\sigma}(r, t)} \sum_{ij} \sum_{l,L} (2L+1) \Lambda_{ji}^{L0}(r, t) \int dr' \frac{r'^l}{r^{l+1}} \Lambda_{ji}^{l0}(r', t) (C_{l0l0}^{00})^2. \quad (6.33)$$

¹This will not be the case when we eventually move to molecules.

²A more detailed explanation of how to do this can be found in appendix C.

³For atoms this is not as bad an approximation as one could a priori believe. The reason for this is because any atomic potential can in the static case be described purely by a $l = 0$ term.

Next we use the fact that we know the CG coefficient in the special case where the third angular quantum number is zero. In that case we have:

$$C_{l_1 m_1 l_2 m_2}^{00} = \delta_{l_1, l_2} \delta_{m_1, -m_2} \frac{(-1)^{l_1 - m_1}}{\sqrt{2j_2 + 1}} \quad (6.34)$$

So in our case we get find: $(C_{l_0 L 0}^{00})^2 = \delta_{lL} / (2L + 1)$. Which we insert to get:

$$\begin{aligned} V_{x,GS,\sigma}^S(\mathbf{r}, t) &= -\frac{1}{\sqrt{4\pi r^2} \rho_{00,\sigma}(r, t)} \sum_{ij} \sum_l \Lambda_{ji}^{l0}(r, t) \int dr' \frac{r'^l}{r_{>}^{l+1}} \Lambda_{ji}^{l0}(r', t) \\ &= -\frac{1}{r^2 \rho_{00,\sigma}(r, t)} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \sum_{j=1}^{N_{\sigma}} \sum_{l=0}^{l_{max}} \Lambda_{ji}^{l0}(r, t) \int dr' \frac{r'^l}{r_{>}^{l+1}} \Lambda_{ji}^{l0}(r', t) Y_{00}. \end{aligned} \quad (6.35)$$

The above expression is easy to calculate numerically.

6.5.2 Spin-dependent screening-response potential, $V_x^R(\mathbf{r}, t)$

Now we calculate the spin-dependent screening-response potential.

We assume a closed shell system, which enables us to use the screening-response potential found in (3.67)¹:

$$V_x^R(\mathbf{r}, t) = \sum_{\sigma} \sum_{i=1}^{N_{\sigma}-1} \frac{\rho_{i\sigma}(\mathbf{r}, t)}{\rho(\mathbf{r}, t)} Q_{i\sigma}(t). \quad (3.67)$$

so the spin-dependent potential is given as:

$$V_{x,\sigma}^R(\mathbf{r}, t) = \sum_{i=1}^{N_{\sigma}-1} \frac{\rho_{i\sigma}(\mathbf{r}, t)}{\rho_{\sigma}(\mathbf{r}, t)} Q_{i\sigma}(t). \quad (6.36)$$

The screening-response potential contains the structure which the screening potential lacks as we shall see in section 7.2. It is a small correction, and it is believed to be strictly positive².

Initially we ignore $Q_{i\sigma}(t)$ and convert the rest to reduced spherical harmonics. In (6.14) an expression for $\rho_{i\sigma}(\mathbf{r}, t)$ is given, when inserted

¹For an open shell system use (3.66). The only difference is whether or not N_{σ} is included in the sum.

²Unfortunately I have been unable to find any source to back up this statement.

we get:

$$\begin{aligned}
V_{x,\sigma}^R(\mathbf{r}, t) &= \frac{1}{\rho_\sigma(\mathbf{r}, t)} \sum_{i=1}^{N_\sigma-1} Q_{i\sigma}(t) \\
&= \frac{1}{\sqrt{4\pi r^2}} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ii}^{LM}(r, t) Y_{LM}(\Omega) \\
&= \frac{1}{\sqrt{4\pi r^2} \rho_\sigma(\mathbf{r}, t)} \sum_{i=1}^{N_\sigma-1} Q_{i\sigma}(t) \sum_{LM} \sqrt{2L+1} \Lambda_{ii}^{LM}(r, t) Y_{LM}(\Omega).
\end{aligned} \tag{6.37}$$

Just like with the screening potential the inverse spin-density complicates the calculation. Once again we make the assumption that all terms with $l > 0$ is neglected. So we only take the angular independent term of our $\rho_\sigma(\mathbf{r}, t)$ expansion as given in (6.17), when inserted we get:

$$\begin{aligned}
V_{x,\sigma}^R(\mathbf{r}, t) &= \frac{1}{\sqrt{4\pi r^2} \rho_{00,\sigma}(r, t) Y_{00}} \sum_{i=1}^{N_\sigma-1} Q_{i\sigma}(t) \Lambda_{ii}^{00}(r, t) Y_{00} \\
&= \frac{1}{r^2 \rho_{00,\sigma}(r, t)} \sum_{i=1}^{N_\sigma-1} Q_{i\sigma}(t) \Lambda_{ii}^{00}(r, t) Y_{00}.
\end{aligned} \tag{6.38}$$

Now we turn our focus to $Q_{i\sigma}(t)$.

In (3.73) we showed that $Q_{i\sigma}(t)$ can be found by solving a matrix equation, a corresponding spin-dependent matrix equation is given as:

$$\sum_{j=1}^{N_\sigma-1} (\delta_{ij} - M_{ji,\sigma}(t)) Q_{j\sigma}(t) = \langle V_{x,\sigma}^S(t) \rangle_{i\sigma} - \langle u_{x,i\sigma}(t) \rangle_{i\sigma}. \tag{6.39}$$

So in order to find $Q_{i\sigma}(t)$, we need to find expressions for $M_{ji,\sigma}(t)$, $\langle V_{x,\sigma}^S(t) \rangle_{i\sigma}$ and $\langle u_{x,i\sigma}(t) \rangle_{i\sigma}$.

We start by calculating $M_{ji,\sigma}(t)$

In (3.71) $M_{ji}(t)$ was defined, its spin-dependent counterpart is then given as:

$$M_{ji,\sigma} = \int d\mathbf{r} \frac{|\varphi_{j\sigma}(\mathbf{r})|^2 |\varphi_{i\sigma}(\mathbf{r})|^2}{\rho_\sigma(\mathbf{r})}. \tag{6.40}$$

An expression for $|\varphi_{j\sigma}(\mathbf{r}, t)|^2$ is given in (6.14), when inserted we get:

$$\begin{aligned}
M_{ji,\sigma}(t) &= \int d\mathbf{r} \frac{1}{4\pi r^4 \rho_\sigma(\mathbf{r}, t)} \sum_{L=0}^{l_{\max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{jj}^{LM*}(r, t) Y_{LM}^*(\Omega) \\
&\quad \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l \sqrt{2l+1} \Lambda_{ii}^{lm}(r, t) Y_{lm}(\Omega) \\
&= \frac{1}{4\pi} \sum_{LM,lm} \sqrt{2L+1} \sqrt{2l+1} \int d\mathbf{r} \frac{1}{r^4 \rho_\sigma(\mathbf{r}, t)} \Lambda_{jj}^{LM*}(r, t) \Lambda_{ii}^{lm}(r, t) \\
&\quad Y_{LM}^*(\Omega) Y_{lm}(\Omega).
\end{aligned} \tag{6.41}$$

Remember our assumption about dropping all terms with $l > 0$. By using this the inverse spin-density is once again converted to its angular independent term. When inserted we get:

$$\begin{aligned}
M_{ji,\sigma}(t) &= \frac{1}{4\pi} \sum_{LM,lm} \sqrt{2L+1} \sqrt{2l+1} \\
&\quad \int d\mathbf{r} \frac{1}{r^4 \rho_{00,\sigma}(r, t) Y_{00}} \Lambda_{jj}^{LM*}(r, t) \Lambda_{ii}^{lm}(r, t) Y_{LM}^*(\Omega) Y_{lm}(\Omega).
\end{aligned} \tag{6.42}$$

The integral is split in radial and angular parts:

$$\begin{aligned}
M_{ji,\sigma}(t) &= \frac{1}{\sqrt{4\pi}} \sum_{LM,lm} \sqrt{2L+1} \sqrt{2l+1} \\
&\quad \int dr \frac{1}{r^2 \rho_{00,\sigma}(r, t)} \Lambda_{jj}^{LM*}(r, t) \Lambda_{ii}^{lm}(r, t) \int d\Omega Y_{LM}^*(\Omega) Y_{lm}(\Omega).
\end{aligned} \tag{6.43}$$

The spherical harmonics are orthonormal to each other as seen in (A.5), when used we get:

$$\begin{aligned}
M_{ji,\sigma}(t) &= \frac{1}{\sqrt{4\pi}} \sum_{LM,lm} \sqrt{2L+1} \sqrt{2l+1} \\
&\quad \int dr \frac{1}{r^2 \rho_{00,\sigma}(r, t)} \Lambda_{jj}^{LM*}(r, t) \Lambda_{ii}^{lm}(r, t) \delta_{Ll} \delta_{Mm} \\
&= \frac{1}{\sqrt{4\pi}} \sum_{LM} (2L+1) \int dr \frac{1}{r^2 \rho_{00,\sigma}(r, t)} \Lambda_{jj}^{LM*}(r, t) \Lambda_{ii}^{LM}(r, t).
\end{aligned} \tag{6.44}$$

So finally we find the expression:

$$M_{ji,\sigma}(t) = \frac{1}{\sqrt{4\pi}} \sum_{L=0}^{l_{\max}} \sum_{M=-L}^L (2L+1) \int dr \frac{1}{r^2 \rho_{00,\sigma}(r, t)} \Lambda_{jj}^{LM*}(r, t) \Lambda_{ii}^{LM}(r, t). \tag{6.45}$$

Reordering the integral and the summation might make the calculation numerically faster:

$$M_{ji,\sigma}(t) = \frac{1}{\sqrt{4\pi}} \int dr \frac{1}{r^2 \rho_{00,\sigma}(r, t)} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L (2L+1) \Lambda_{jj}^{LM*}(r, t) \Lambda_{ii}^{LM}(r, t). \quad (6.46)$$

Next we calculate $\langle u_{xi\sigma}(t) \rangle_{i\sigma}$

In (3.74) we have an expression for $u_{xi\sigma}(\mathbf{r}, t)$:

$$u_{xi\sigma}(\mathbf{r}, t) = - \sum_{j=1}^{N_\sigma} \frac{\varphi_{j\sigma}^*(\mathbf{r}, t)}{\varphi_{i\sigma}^*(\mathbf{r}, t)} \int d^3r' \frac{\varphi_{i\sigma}^*(\mathbf{r}', t) \varphi_{j\sigma}(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (6.47)$$

The integral is calculated in (6.26), by insertion we get:

$$u_{xi\sigma}(\mathbf{r}, t) = - \sum_{j=1}^{N_\sigma} \frac{\varphi_{j\sigma}^*(\mathbf{r}, t)}{\varphi_{i\sigma}^*(\mathbf{r}, t)} \sqrt{4\pi} \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \frac{1}{\sqrt{2l+1}} \int dr' \frac{r'^l}{r^{l+1}} \Lambda_{ji}^{lm}(r', t) Y_{lm}(\Omega). \quad (6.48)$$

Because of the orbital in the denominator it is very limited what we can do to the above expression, luckily what we are really interested in is its spatial mean as defined in (3.53). The spatial mean of the above is given as:

$$\begin{aligned} \langle u_{xi\sigma}(t) \rangle_{i\sigma} &= - \int d\mathbf{r} |\varphi_{i\sigma}(\mathbf{r}, t)|^2 u_{xi\sigma}(\mathbf{r}, t) \\ &= - \int d\mathbf{r} |\varphi_{i\sigma}(\mathbf{r}, t)|^2 \sum_{j=1}^{N_\sigma} \frac{\varphi_{j\sigma}^*(\mathbf{r}, t)}{\varphi_{i\sigma}^*(\mathbf{r}, t)} \sqrt{4\pi} \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \frac{1}{\sqrt{2l+1}} \\ &\quad \int dr' \frac{r'^l}{r^{l+1}} \Lambda_{ji}^{lm}(r', t) Y_{lm}(\Omega) \\ &= - \sqrt{4\pi} \sum_{j=1}^{N_\sigma} \sum_{lm} \frac{1}{\sqrt{2l+1}} \int d\mathbf{r} [\varphi_{i\sigma}^*(\mathbf{r}, t) \varphi_{j\sigma}(\mathbf{r}, t)]^* \\ &\quad \int dr' \frac{r'^l}{r^{l+1}} \Lambda_{ji}^{lm}(r', t) Y_{lm}(\Omega). \end{aligned} \quad (6.49)$$

In (6.14) $\varphi_{i\sigma}^*(\mathbf{r}, t)\varphi_{j\sigma}(\mathbf{r}, t)$ is calculated. When inserted we get:

$$\begin{aligned} \langle u_{xi\sigma}(t) \rangle_{i\sigma} &= -\sqrt{4\pi} \sum_{j=1}^{N_\sigma} \sum_{lm} \frac{1}{\sqrt{2l+1}} \int d\mathbf{r} \\ &\left[\frac{1}{\sqrt{4\pi r^2}} \sum_{L=0}^{l_{max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ji}^{LM}(r, t) Y_{LM}(\Omega) \right]^* \\ &\int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t) Y_{lm}(\Omega). \end{aligned} \quad (6.50)$$

The terms are reordered and the integral is split in angular and radial part:

$$\begin{aligned} \langle u_{xi\sigma}(t) \rangle_{i\sigma} &= - \sum_{j=1}^{N_\sigma} \sum_{lm, LM} \frac{\sqrt{2L+1}}{\sqrt{2l+1}} \int dr \\ &\Lambda_{ji}^{LM*}(r, t) \int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t) \int d\Omega Y_{LM}^*(\Omega) Y_{lm}(\Omega). \end{aligned} \quad (6.51)$$

The spherical harmonics are othornormal to each other as seen in (A.5), when used we get:

$$\begin{aligned} \langle u_{xi\sigma}(t) \rangle_{i\sigma} &= - \sum_{j=1}^{N_\sigma} \sum_{lm, LM} \frac{\sqrt{2L+1}}{\sqrt{2l+1}} \\ &\int dr \Lambda_{ji}^{LM*}(r, t) \int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t) \delta_{Ll} \delta_{Mm}. \end{aligned} \quad (6.52)$$

By using the delta-functions we end up with the following expression:

$$\langle u_{xi\sigma}(t) \rangle_{i\sigma} = - \sum_{j=1}^{N_\sigma} \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \int dr \Lambda_{ji}^{lm*}(r, t) \int dr' \frac{r'^l}{r'^{l+1}} \Lambda_{ji}^{lm}(r', t). \quad (6.53)$$

Finally $\langle V_{x,\sigma}^S(t) \rangle_{i\sigma}$ is found

We make this calculation very simple by using the fact that the spin-dependent screening potential $V_{x,\sigma}^S(\mathbf{r}, t)$ is directly needed in order to calculate the exchange potential. This means that we already have the spin-dependent screening potential $V_{x,\sigma}^S(\mathbf{r}, t)$ stored in our code. Hence we have:

$$V_{x,\sigma}^S(\mathbf{r}, t) = \sum_{l=0}^{l_{max}} \sum_{m=-l}^l V_{x,\sigma lm}^S(r, t) Y_{lm}(\Omega). \quad (6.54)$$

We start by taking the spatial mean of our screening potential, as defined in (3.53), this gives us:

$$\langle V_{x,\sigma}^S(t) \rangle_{i\sigma} = \int d^3r |\varphi_{i\sigma}(\mathbf{r}, t)|^2 V_{x,\sigma}^S(\mathbf{r}, t). \quad (6.55)$$

In (6.14) $|\varphi_{i\sigma}(\mathbf{r}, t)|^2$ is calculated, note we can freely choose the complex conjugate of the expression due to its form, which we do. When inserted we get:

$$\begin{aligned}\langle V_{x,\sigma}^S(t) \rangle_{i\sigma} &= \int d^3r V_{x,\sigma}^S(\mathbf{r}, t) \frac{1}{\sqrt{4\pi r^2}} \sum_{L=0}^{l_{\max}} \sum_{M=-L}^L \sqrt{2L+1} \Lambda_{ii}^{LM*}(r, t) Y_{LM}^*(\Omega) \\ &= \frac{1}{\sqrt{4\pi}} \sum_{LM} \sqrt{2L+1} \int d^3r \frac{1}{r^2} V_{x,\sigma}^S(\mathbf{r}, t) \Lambda_{ii}^{LM*}(r, t) Y_{LM}^*(\Omega).\end{aligned}\quad (6.56)$$

Next we insert (6.54):

$$\begin{aligned}\langle V_{x,\sigma}^S(t) \rangle_{i\sigma} &= \frac{1}{\sqrt{4\pi}} \sum_{LM} \sqrt{2L+1} \int d^3r \frac{1}{r^2} \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l \\ &V_{x,\sigma lm}^S(r, t) Y_{lm}(\Omega) \Lambda_{ii}^{LM*}(r, t) Y_{LM}^*(\Omega).\end{aligned}\quad (6.57)$$

The integral is split in radial and angular parts:

$$\begin{aligned}\langle V_{x,\sigma}^S(t) \rangle_{i\sigma} &= \frac{1}{\sqrt{4\pi}} \sum_{LM, lm} \sqrt{2L+1} \int dr V_{x,\sigma lm}^S(r, t) \Lambda_{ii}^{LM*}(r, t) \\ &\int d\Omega Y_{lm}(\Omega) Y_{LM}^*(\Omega).\end{aligned}\quad (6.58)$$

The spherical harmonics are orthonormal to each other as seen in (A.5), when used we get:

$$\begin{aligned}\langle V_{x,\sigma}^S(t) \rangle_{i\sigma} &= \frac{1}{\sqrt{4\pi}} \sum_{LM, lm} \sqrt{2L+1} \int dr V_{x,\sigma lm}^S(r, t) \Lambda_{ii}^{LM*}(r, t) \delta_{lL} \delta_{mM} \\ &= \frac{1}{\sqrt{4\pi}} \sum_{l=0}^{l_{\max}} \sum_{m=-l}^l \sqrt{2l+1} \int dr V_{x,\sigma lm}^S(r, t) \Lambda_{ii}^{lm*}(r, t).\end{aligned}\quad (6.59)$$

This was the last component we needed in order to calculate the screening response potential.

6.6 The nuclei potential, V_{en}

In this section we calculate the electron-nuclei attraction.

For the record it should be stated that origo is always placed at the center-of-mass.

The calculations are split in several cases, depending on the complexity of the problem¹.

6.6.1 Single atom

In this trivial case we only have one atom. So the system is spherical symmetric, and hence we get:

$$V_{en}(r) = -\frac{Z}{r}. \quad (6.60)$$

In order to get this into the spherical harmonic basis we use the fact that first spherical harmonic is angular independent. The first spherical harmonic is given as:

$$Y_{00} = \frac{1}{\sqrt{4\pi}}. \quad (6.61)$$

So our potential is converted to a spherical harmonic basis as follows:

$$V_{en}(r) = -\sqrt{4\pi}\frac{Z}{r}Y_{00}. \quad (6.62)$$

6.6.2 Diatomic homo

Next up we consider a diatomic homo.

Our potential is given as:

$$V_{en}(\mathbf{r}) = -Z \left(\frac{1}{|\mathbf{r} - \mathbf{R}/2|} + \frac{1}{|\mathbf{r} + \mathbf{R}/2|} \right). \quad (6.63)$$

We chose our coordinate system such that both atoms lie on the z-axis, hence the system is independent of the azimuthal angle φ .

To get started we turn to one of the relations in the appendix, namely (A.7) which states:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{(r_{<})^l}{(r_{>})^{l+1}} Y_{lm}^*(\theta, \varphi) Y_{lm}(\theta', \varphi'). \quad (A.7)$$

By insertion we get:

$$V_{en}(\mathbf{r}) = -Z \sum_{lm} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} [Y_{lm}(\theta, \varphi) Y_{lm}^*(\theta_1, \varphi_1) + Y_{lm}(\theta, \varphi) Y_{lm}^*(\theta_2, \varphi_2)]. \quad (6.64)$$

¹In principle the last case can reproduce all the others.

Now we use the fact that the atoms are placed in the z-axis and origo is the center of mass. From this we know that: $\theta_1 = 0 = \theta_2 + \pi$, which when inserted gives us:

$$V_{en}(\mathbf{r}) = -Z \sum_l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l0}(\theta, \varphi) [Y_{l0}^*(0, \varphi_1) + Y_{l0}^*(\pi, \varphi_2)]. \quad (6.65)$$

Now we use the parity relation for spherical harmonics as given in (A.11), which gives us:

$$V_{en}(\mathbf{r}) = -Z \sum_l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l0}(\theta, \varphi) \left[Y_{l0}^*(0, \varphi_1) + (-1)^l Y_{l0}^*(0, \varphi_2) \right]. \quad (6.66)$$

Remember that our atoms are azimuthal independent, hence we can freely set $\varphi_1 = \varphi_2$. This makes all the odd terms terminate, and we are left with all the even terms:

$$V_{en}(\mathbf{r}) = -2Z \sum_l \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l0}(\theta, \varphi) Y_{l0}^*(0, \varphi_1). \quad (6.67)$$

Finally we use the fact that $Y_{lm}(0, \varphi) = \sqrt{\frac{2l+1}{4\pi}} \delta_{m0}$ as given in (A.8):

$$V_{en}(\mathbf{r}) = -2Z \sum_l \sqrt{\frac{4\pi}{2l+1}} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{l0}(\theta, \varphi). \quad (6.68)$$

6.6.3 Arbitrary cylinder symmetric potential

Finally we move on to the general case which can reproduce all the others.

We assume a string of n different atoms, j of the atoms are lying above origo, while the rest are lying below. An illustration for $n = 3, j = 2$ is given in figure 6.1.

Again we start with:

$$V_{en}(\mathbf{r}) = - \sum_{i=1}^N \frac{Z_i}{|\mathbf{r} - \mathbf{R}_i|}, \quad (6.69)$$

and using the expansion given in (A.7) we get:

$$V_{en}(\mathbf{r}) = - \sum_{i=1}^N \sum_{l=0}^{l_{max}} \sum_{m=-l}^l Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} \frac{4\pi}{2l+1} Y_{lm}(\theta, \varphi) Y_{lm}^*(\theta_i, \varphi_i). \quad (6.70)$$

We use the cylinder symmetry to set $m = 0 =$ and $\varphi_i = 0$:

$$V_{en}(\mathbf{r}) = - \sum_{i=1}^N \sum_{l=0}^{l_{max}} Z_i \frac{4\pi}{2l+1} \frac{r_{i<}^l}{r_{i>}^{l+1}} Y_{l0}(\theta, \varphi) Y_{l0}^*(\theta_i, 0). \quad (6.71)$$

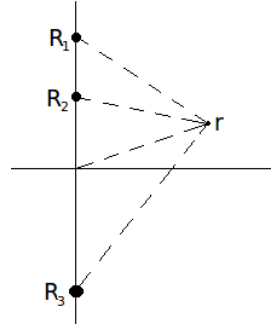


Figure 6.1: R_1 and R_2 is lying above origo and hence θ_1 and $\theta_2 = 0$ while R_3 is lying below which makes $\theta_3 = \pi$

The sum is split in two parts, one lying above origo and one below:

$$V_{en}(\mathbf{r}) = - \sum_{l=0}^{l_{max}} \frac{4\pi}{2l+1} Y_{l0}(\theta, \varphi) \left[\sum_{i=1}^j Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} Y_{l0}^*(0,0) + \sum_{i=j+1}^N Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} Y_{l0}^*(\pi,0) \right]. \quad (6.72)$$

Now we use the parity relation for spherical harmonics as given in (A.11), which gives us:

$$V_{en}(\mathbf{r}) = - \sum_{l=0}^{l_{max}} \frac{4\pi}{2l+1} Y_{l0}(\theta, \varphi) \left[\sum_{i=1}^j Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} Y_{l0}^*(0,0) + \sum_{i=j+1}^N Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} (-1)^l Y_{l0}^*(0,0) \right]. \quad (6.73)$$

We use the fact that $Y_{l0}(0,0) = \sqrt{\frac{2l+1}{4\pi}}$:

$$V_{en}(\mathbf{r}) = - \sum_{l=0}^{l_{max}} \sqrt{\frac{4\pi}{2l+1}} Y_{l0}(\theta, \varphi) \left[\sum_{i=1}^j Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} + \sum_{i=j+1}^N Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} (-1)^l \right]. \quad (6.74)$$

Finally we split the two terms in even and odd angular quantum numbers. This enables us to collect the terms:

$$V_{en}(\mathbf{r}) = - \sum_{l=0, \text{even}}^{l_{max}} \sqrt{\frac{4\pi}{2l+1}} Y_{l0}(\theta, \varphi) \sum_{i=1}^N Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} - \sum_{l=1, \text{odd}}^{l_{max}} \sqrt{\frac{4\pi}{2l+1}} Y_{l0}(\theta, \varphi) \left[\sum_{i=1}^j Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} - \sum_{i=j+1}^N Z_i \frac{r_{i<}^l}{r_{i>}^{l+1}} \right]. \quad (6.75)$$

Hence we now have an expression which can create the electron-nucleus potential of any atom, or line of atoms.

Chapter 7

Results

In this chapter we will look at results from our simulations on different simple atomic systems.

Our simulations are done on a grid consisting of 2048 equidistant radial grid points spread from zero to 100 au. Our angular basis is set sufficiently high¹.

So far we have only considered atomic systems. For a general atomic system we use the following spin-dependent potential:

$$V_{\sigma}(\mathbf{r}, t) = V_{en}(r) + V_H(\mathbf{r}, t) + V_{x,\sigma}^{KLI}(\mathbf{r}, t) \quad (7.1)$$

where $V_{en}(r)$ is the electron-nucleus interaction, which was covered in section 6.6, $V_H(\mathbf{r}, t)$ is the Hartree interaction which was covered in section 6.4 finally we have the exchange potential, $V_{x,\sigma}^{KLI}(\mathbf{r}, t)$ as covered in section 6.5.

The two atomic systems we have investigated thoroughly and those are helium and beryllium. The reason why we have studied those two systems is that they are both closed shell systems, with helium being the simplest atomic system where DFT becomes relevant, and beryllium the second simplest.

7.1 Helium

Ground state helium is spherical symmetric, and consists of two electrons, which occupy the two spin-states in the 1S-orbital.

The potential for helium is of the form given in (7.1). However it should be noted that in helium the exchange potential is particularly simple, since the screening-response potential is zero. This can be

¹For helium and beryllium which we cover here, it is sufficient to take a single spherical harmonic since the lowest angular quantum number does not spread to others. For more complicated systems the angular orbitals will slowly contaminate other orbitals, hence it is necessary to use two to three times as many spherical harmonics as the system contains.

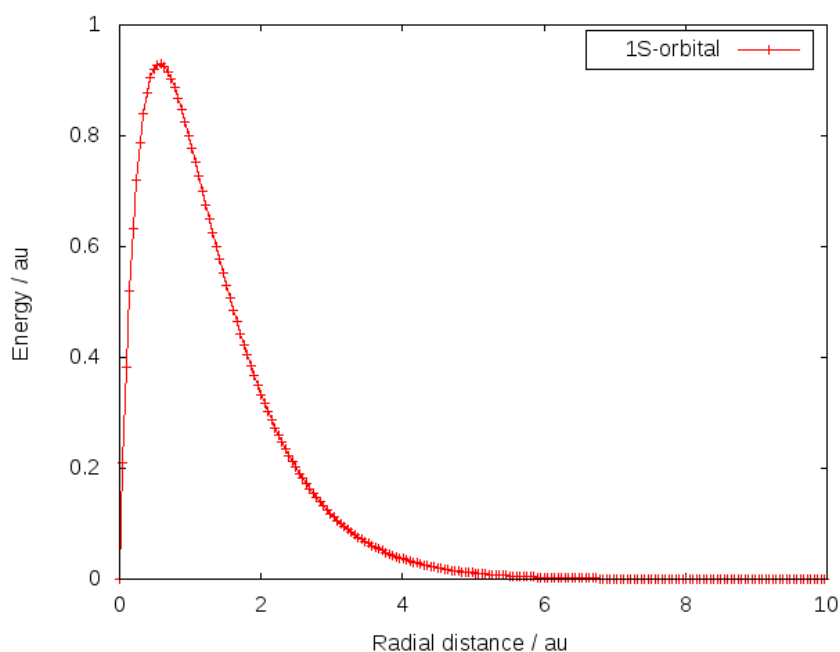


Figure 7.1: Here we see the 1S reduced orbital for helium. It looks just like the normal 1S reduced wavefunction, just as expected.

attributed to the fact that we do not sum over the outermost electrons when creating the potential, but for helium this leaves no electrons to create the potential from and hence we get zero contribution from the screening-response potential.

A run of helium to a convergence accuracy of $5 \cdot 10^{-10}$ takes roughly 15000 iterations, which on our cluster can be done in less than two minutes. The ionisation energy of helium is found to be: $E = -0.915$ au. An ionization comparison between our simulations and others is given in table 7.1 on page 87.

The resulting reduced orbital can be seen in figure 7.1. The different potentials are shown in figure 7.2-7.4. Finally figure 7.5 shows that the nucleus potential exactly cancel the Hartree potential in the asymptotic limit¹, leaving the screening exchange potential the only long-range potential.

¹This asymptotic cancelling is to be expected. In the asymptotic limit the Hartree potential simplifies to the same form as the nucleus potential, and since we know that the total charge in the electrons exactly negates the charge in the nucleus this negation should also happen when combining the potentials.

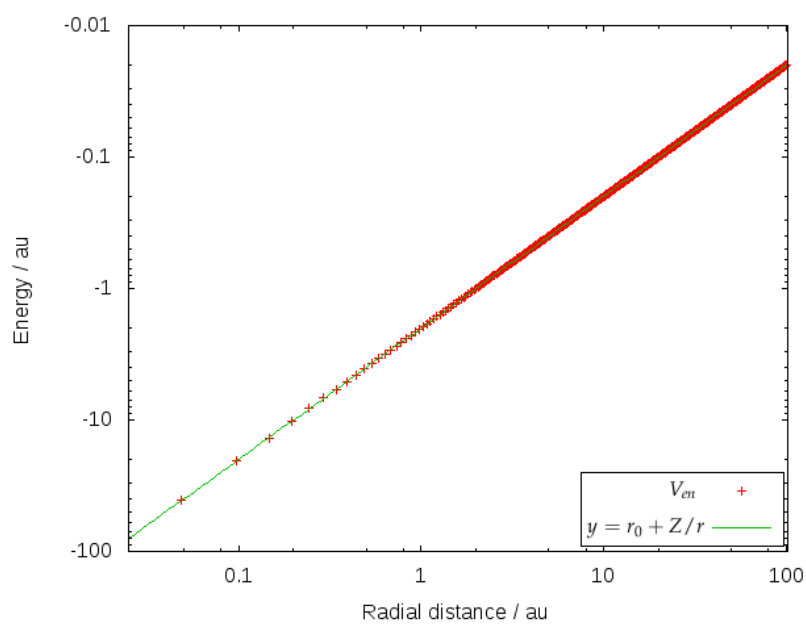


Figure 7.2: Here we see the electron-nucleus potential of helium. The fitting parameters are $Z = -2.00$ and $r_0 = 0.00$. This potential is static and explicitly created this way, hence the form and values should come as no surprise.

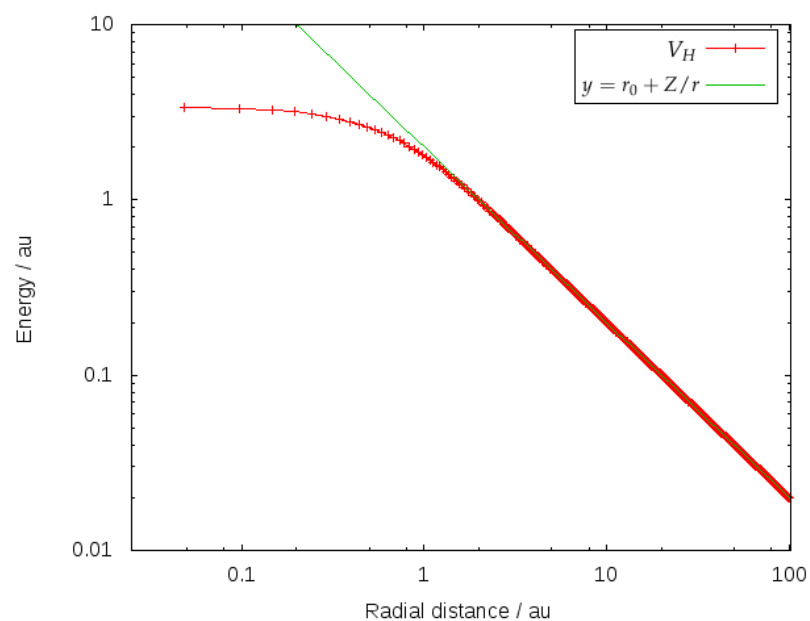


Figure 7.3: Here we see the Hartree potential for helium. The asymptotic fitting parameters are $Z = 2.00$ and $r_0 = 0.00$. Unlike the nucleus potential this is dynamic since it depends upon the electron density.

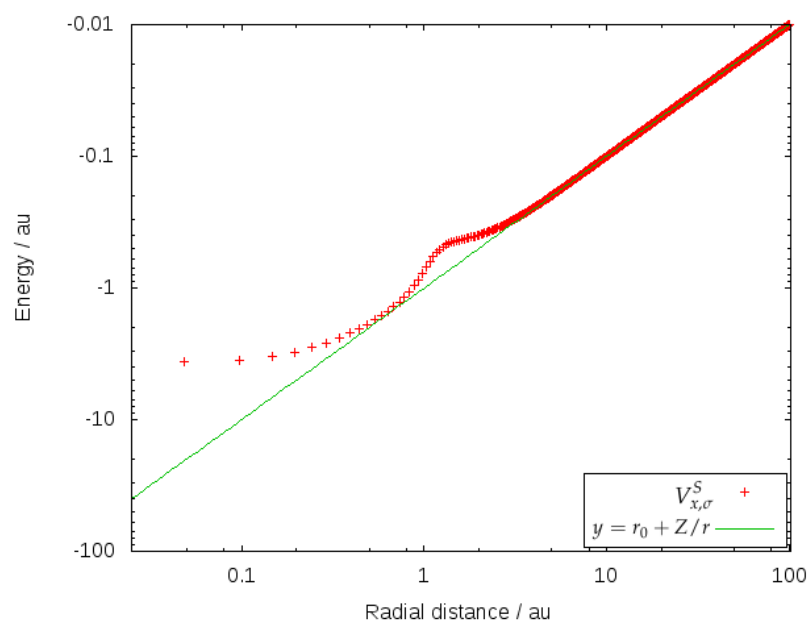


Figure 7.4: Here we see the exchange potential for helium. The asymptotic fitting parameters are $Z = -1.00$ and $r_0 = 0.00$, meaning that the asymptotic tail is seen to fall as $-1/r$ just as expected.

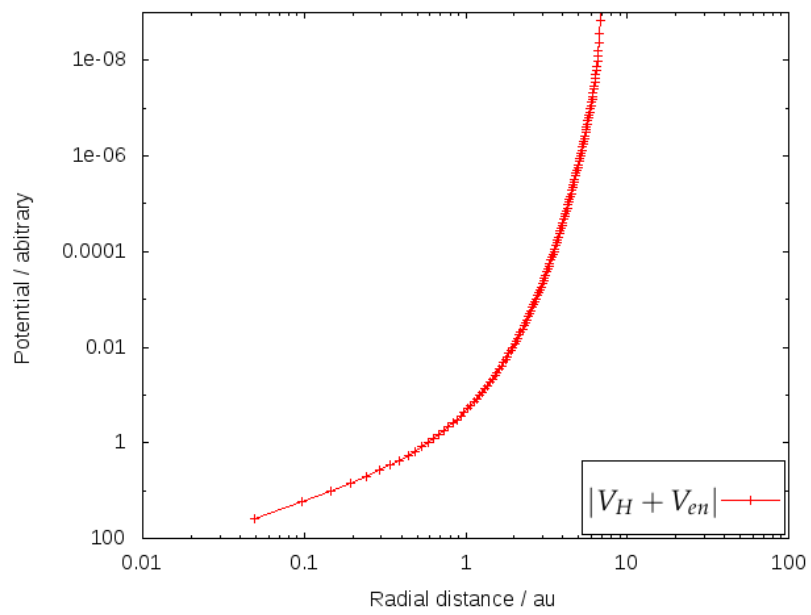


Figure 7.5: Here we see the absolute sum of the nucleus potential and the Hartree potential. We see that the two potentials cancel each other in the asymptotic region, just as expected.

7.2 Beryllium

Beryllium consist of one nucleus and four electrons, two electrons in 1S-states and two electrons in 2S-states.

The potential for beryllium is of the form given in (7.1).

A run of beryllium to a convergence accuracy of $5 \cdot 10^{-10}$ takes roughly 5000 iterations, which on our cluster is done in less than two minutes. The ionisation energy of beryllium is found to be: $E = -0.314$ au, while the 1S state is bound with an energy of $E = -4.283$ au. An ionization comparison between our simulations and others is given in table 7.1 on page 87.

The resulting reduced orbitals can be seen in figure 7.6 & 7.7. The different potentials are shown in figure 7.8-7.9. For comparison the OEP/KLI potential from [38] is shown in figure 7.10.

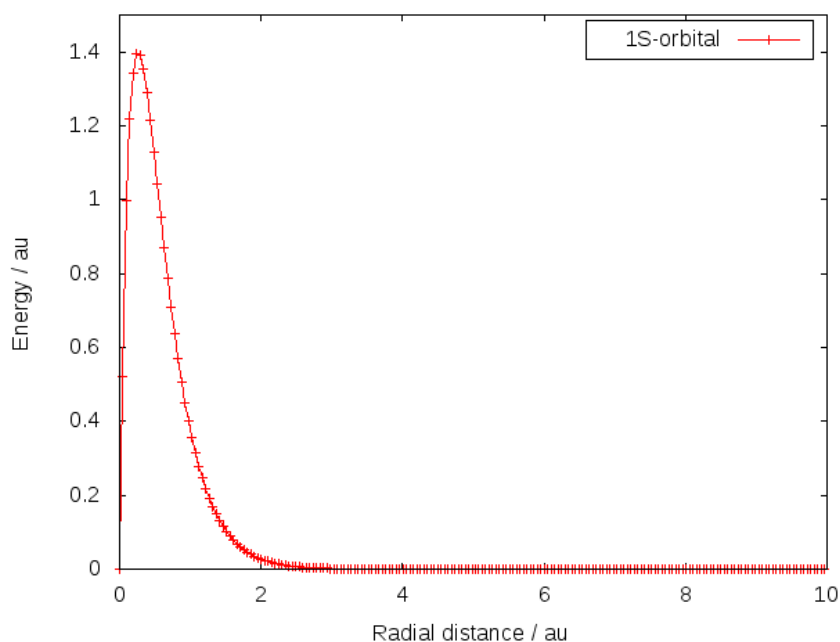


Figure 7.6: Here we see the 1S reduced orbital for Beryllium, the shape is as expected. If we compare it with the helium orbital, we see that the orbital has been shifted closer to the nucleus, which is to be expected due to the more attractive nucleus. For this atom the grid points are still sufficiently packed to accurately emulate the orbital structure. But for larger atoms these inner orbitals could become problematic.

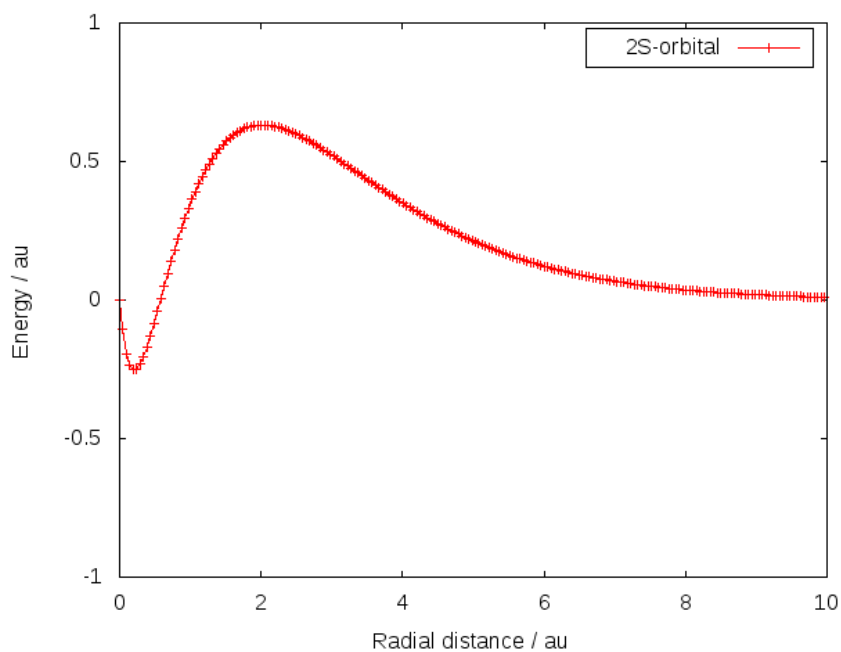


Figure 7.7: Here we see the 2S reduced orbital for Beryllium, the shape is as expected for a 2S orbital.

Table 7.1: Comparison of ionisation energies for different methods. LSDA, stands for local-spin density approximation, our method is the KLI method, while HF is the Hartree-Fock method and finally exp is the experimental results. The references are taken from [39].

Atom	LSDA	KLI	HF	exp
He	0.517	0.915	0.918	0.904
Be	0.170	0.314	0.309	0.343

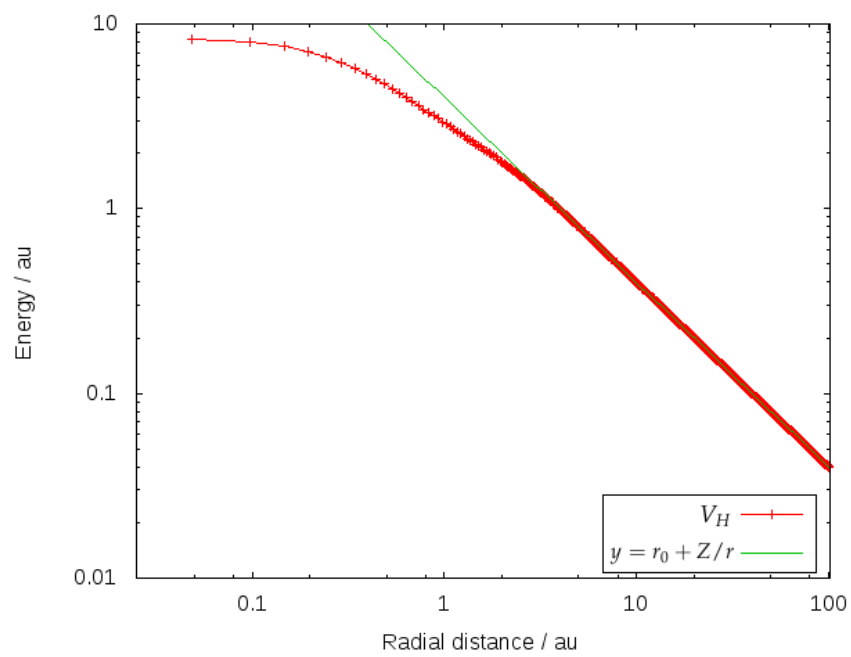


Figure 7.8: Here we see the Hartree potential for Beryllium. The asymptotic fitting parameters are $Z = 4.00$ and $r_0 = 0.00$, as expected.

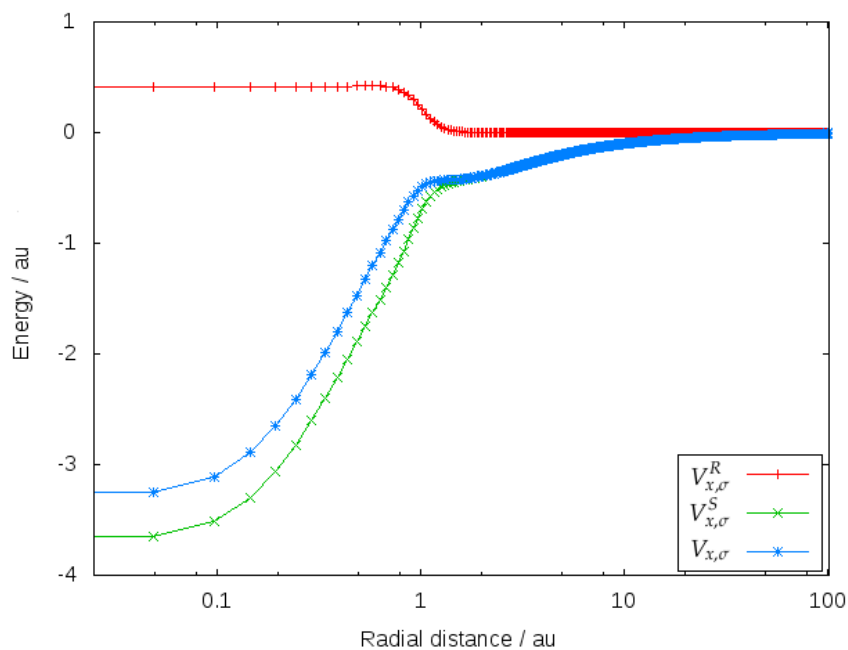


Figure 7.9: Here we see the exchange potential for beryllium. The screening potential is much like the one shown for helium except a change in the steepness, but we also see the screening response potential. The screening-response potential is constant within a region corresponding to an electronic shell, but changes abruptly in the boundary region between shells. The step in the screening-response potential corresponds to a transition in the dominant electron shell from 1S to 2S as confirmed by figure 7.6 & 7.7. Compared to the response potential, we see that the screening-response potential is a short-range potential, containing structural information about the system.

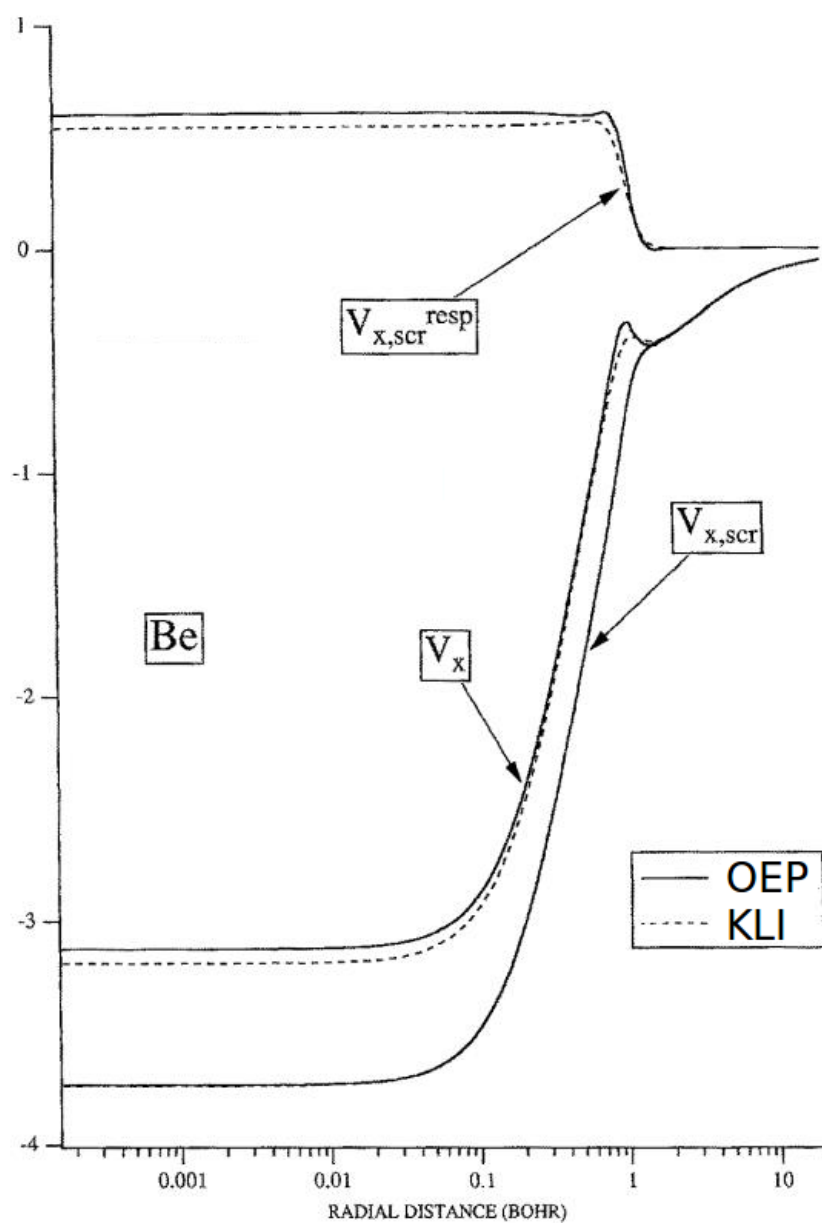


Figure 7.10: Here we have a graph from [38], showing not only the KLI exchange potential, but also the OEP exchange potential for beryllium. As we can see the error made by making the KLI approximation is small, further we see that their KLI potential is identical to the one we find.

Chapter 8

Conclusion

The end goal of this project is to make an effective parallel program, which using adiabatic time-dependent density functional theory, is able to simulate atoms and molecules. These goals were made on a somewhat naive ground, with no actual knowledge within the field of density functional theory, and it quickly became apparent to us that they were not realistic goals for a single master project with no prior knowledge of density functional theory.

So what we have created is a guide, which hopefully should make my successor able to reach the end goal, and avoid all the dead ends we have already explored.

In this thesis we have discussed why the direct Schrödinger approach is not computational feasible. We have created density functional theory, in what I believe is the most intuitive way. To make density functional theory workable in practice we introduced the Kohn-Sham method. From this we naturally encountered the exchange-correlation energy functionals, which we proceeded to give a thorough overview of¹. After the overview of the exchange-correlation energy functionals, we then devoted our attention to the exact exchange energy functional, whose potential we found an integral equation for, which we turned into a regular equation by use of the KLI-approximation.

As a finalisation of the general theory we then introduced time-dependent density functional theory, where we quickly made the adiabatic approximation, which enabled us to use the time-independent theories and functionals in the time-dependent domain.

Finally we turned to the numerical aspect of creating the simulator. Several parallelisation schemes were discussed. Numerical methods to finding the initial states were discussed and imaginary time propagation was in the end chosen. It was mentioned that, due to numerical

¹As thorough as possible without introducing the complicated exchange-correlation hole.

speed our code uses a spherical harmonic basis. The boost in speed this gives us, comes at the cost of having to convert every relevant expression to a spherical harmonic basis.

As a proof of concept we have shown results for those systems which our code currently work on. In the case of beryllium, our data is matched with data from other simulations using the same potentials. So far our code has shown to not only be fast, but also accurate. In fact the accuracy of our method has thus far proved even more accurate than the much more numerically demanding Hartree-Fock method.

In the end, having a time-dependent density functional theory simulator as opposed to a single-active electron Schrödinger equation solver, would give more realistic simulations of a lot of interesting systems, which is sorely needed, in order for theoretical physics to catch up and qualitatively explain all the interesting phenomena that experimental laser physicist can produce today.

8.1 Future perspective

The idea for the immediate future of this project, is to get all the closed shell atoms working. When all the closed shell systems have been calculated, the plan is to include non-closed shell atoms. In order to move into the realm of molecules, a few modifications to the exchange potential might be needed, but otherwise it should be straightforward. One thing that could become a problem for larger systems, is the fact that we use an equidistant grid. For larger systems such a grid may not contain enough grid points near the nuclei to accurately capture the structure of these system.

In the end, we hope to be able to simulate any atom or small sized molecule interacting with a strong-field laser. By using theoretical simulations we are not restricted, in the pulse length, like experimental physicists, and hence this could be used to accurately simulate attosecond physics. Further such a simulator would unlock many multi-electron strong-field phenomena, like dynamic multi-channel high-harmonic generation.

Appendix A

Spherical harmonics

Spherical harmonics is the natural basis to describe atomic and molecular systems in. But more than that knowing how to work with spherical harmonics is central for understanding chapter 6. So here we have gathered some of the most frequently used spherical harmonic relations.

The definition of spherical harmonics

The usual definition of spherical harmonics is through the use of associated Legendre functions [40, p. 788]:

$$Y_{lm}(\theta, \varphi) := (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_{lm}(\cos \theta) e^{im\varphi}. \quad (\text{A.1})$$

Writing spherical harmonics out explicitly is going to be ugly. Luckily most things can be done by use of some special relations.

The identity

The simplest trick has to do with angular independent spherical harmonic [40, p. 790]:

$$Y_{00}(\theta, \varphi) = Y_{00} = \frac{1}{\sqrt{4\pi}}. \quad (\text{A.2})$$

From this we get the identity:

$$Y_{00} \sqrt{4\pi} = 1, \quad (\text{A.3})$$

Complex conjugate

The complex conjugate relation is given as [40, p. 796]:

$$Y_{lm}^*(\Omega) = (-1)^m Y_{lm}(\Omega). \quad (\text{A.4})$$

Inner product of two spherical harmonics with same angle

When working with spherical harmonics we often end up using the orthonormality relation[40, p. 788]:

$$\int Y_{l_1 m_1}^*(\Omega) Y_{l_2 m_2}(\Omega) d\Omega = \delta_{l_1, l_2} \delta_{m_1, m_2}. \quad (\text{A.5})$$

Product of spherical harmonics with same angle

Without the integral the above is somewhat more ugly[10, p. 1006]:

$$Y_{l_1 m_1}(\Omega) Y_{l_2 m_2}(\Omega) = \sum_{l=|l_1-l_2|}^{l_1+l_2} \sum_{m=-l}^l \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}} C_{l_1 0 l_2 0}^{l 0} C_{l_1 m_1 l_2 m_2}^{l m} Y_{l m}(\Omega). \quad (\text{A.6})$$

Converting a coulomb denominator

In atomic & molecular physics we often need to convert the coulomb denominator to spherical harmonics[10, 1007]:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{(r_<)^l}{(r_>)^{l+1}} Y_{lm}^*(\Omega) Y_{lm}(\Omega'). \quad (\text{A.7})$$

Zero inclination

In the special case of zero inclination we get:

$$Y_{lm}(0, \varphi) = \sqrt{\frac{2l+1}{4\pi}} \delta_{m0}. \quad (\text{A.8})$$

Parity rule

Another relation we need is the parity rule for spherical harmonics. For associated legendre functions we have the following parity rule[40, p. 776]:

$$P_{lm}(-x) = (-1)^{l+m} P_{lm}(x). \quad (\text{A.9})$$

From (A.1) we find the special case:

$$Y_{l0}(\pi, \varphi) = \sqrt{\frac{2l+1}{4\pi}} P_{l0}(-1). \quad (\text{A.10})$$

By combining this with the parity relation for associated legendre functions (A.9), we find:

$$Y_{l0}(\pi, \varphi) = Y_{l0}(0, \varphi) (-1)^l. \quad (\text{A.11})$$

Appendix B

Radial recurring integral

In this section we focus on solving the general integral:

$$F^L(r) = \int dr' \frac{r_{<}^L}{r_{>}^{L+1}} f(r'), \quad (\text{B.1})$$

where $r_{<} = \min(r, r')$, $r_{>} = \max(r, r')$.

The normal way to do the integral is to split it in the 2 cases:

$$F^L(r) = \int dr' \frac{(r_{<})^L}{(r_{>}^{L+1})} f(r') \quad (\text{B.2})$$

$$= \int_0^r dr' f(r') \frac{(r')^L}{r^{L+1}} + \int_r^\infty dr' f(r') \frac{r^L}{(r')^{L+1}} \quad (\text{B.3})$$

$$= \frac{1}{r^{L+1}} \int_0^r dr' f(r') (r')^L + r^L \int_r^\infty dr' f(r') \frac{1}{(r')^{L+1}}. \quad (\text{B.4})$$

Numerically we can solve it using the trapezoidal rule on a finite grid. The integral around grid point j is given as:

$$F_j^L = \frac{\Delta r}{r_j^{L+1}} \sum_{i=0}^{j-1} f_i(r)_i^L + r_j^L \Delta r \sum_{i=j}^{N_r-1} f_i \frac{1}{(r_i)^{L+1}}. \quad (\text{B.5})$$

If we split the integral we get:

$$F_j^L = \underline{F_j^L} + \overline{F_j^L}, \quad (\text{B.6})$$

where

$$\underline{F_j^L} = \frac{\Delta r}{r_j^{L+1}} \sum_{i=0}^{j-1} f_i(r)_i^L, \quad (\text{B.7})$$

and

$$\overline{F_j^L} = r_j^L \Delta r \sum_{i=j}^{N_r-1} f_i \frac{1}{(r_i)^{L+1}}. \quad (\text{B.8})$$

Both of these expressions can then be made recursively as:

$$\overline{F_{j+1}^L} = \frac{r_j^{L+1}}{r_{j+1}^{L+1}} \overline{F_j^L} + \Delta r f_j \frac{r_j^L}{r_{j+1}^{L+1}}, \quad (\text{B.9})$$

and

$$\overline{F_{j+1}^L} = \frac{r_{j+1}^L}{r_j^L} \overline{F_j^L} - \Delta r f_j \frac{r_{j+1}^L}{r_j^{L+1}}. \quad (\text{B.10})$$

Since we need the integral for all grid points, the recursive method is very efficient, and is the one implemented in the code.

Appendix C

Powers of the density

In section 6.3 the density is found in a spherical harmonic basis, But often we also need powers of the density in the spherical harmonic basis. For instance the LB α 94 exchange potential given in equation (2.26) requires that we calculate $\rho^{1/3}$ and $\rho^{4/3}$.

Remember that since the density is saved in our code, we have:

$$\rho(\mathbf{r}, t) = \sum_{LM} \rho_{LM}(r, t) Y_{LM}(\Omega) \quad (\text{C.1})$$

A direct power approach gives:

$$\rho(\mathbf{r}, t)^{1/3} = \left(\sum_{LM} \rho_{LM}(r, t) Y_{LM}(\Omega) \right)^{1/3}. \quad (\text{C.2})$$

This is no good for two reasons, first we would need a way to move the power inside the sum, which is non trivial. Secondly even if we somehow do move it inside the sum, we would most likely end up with Y_{lm} to some power, hence we would no longer be in the correct basis. Instead another approach is done.

We use the binomial expansion:

$$(1 + x)^{(1/3)} = 1 + \frac{x}{3} - \frac{x^2}{9} + \frac{5x^3}{81} - \frac{10x^4}{243} + \frac{22x^5}{729} - O(x^6) \quad (\text{C.3})$$

which is valid whenever x is close to zero.

By taking the angular independent part of the density given in

(C.1) outside the sum we find:

$$\begin{aligned}
\rho(\mathbf{r}, t) &= \sum_{LM} \rho_{LM}(r, t) Y_{LM}(\Omega) \\
&= \rho_{00}(r, t) Y_{00} + \sum_{LM}^* \rho_{LM}(r, t) Y_{LM}(\Omega) \\
&= \rho_{00}(r, t) Y_{00} \left(1 + \sum_{LM}^* \frac{\rho_{LM}(r, t)}{\rho_{00}(r, t) Y_{00}} Y_{LM}(\Omega) \right) \quad (C.4) \\
&= \rho_{00}(r, t) Y_{00} \tilde{\rho}(\mathbf{r}, t) \\
&= \frac{\rho_{00}(r, t)}{\sqrt{4\pi}} \tilde{\rho}(\mathbf{r}, t)
\end{aligned}$$

where * means that $L = 0$ and $M = 0$ is excluded from the sum.

Taking the density to the 1/3 power gives us:

$$\begin{aligned}
\rho^{1/3}(\mathbf{r}, t) &= \left(\frac{\rho_{00}(r, t)}{\sqrt{4\pi}} \tilde{\rho}(\mathbf{r}, t) \right)^{1/3} \\
&= \left(\frac{\rho_{00}(r, t)}{\sqrt{4\pi}} \right)^{1/3} \tilde{\rho}^{1/3}(\mathbf{r}, t), \quad (C.5)
\end{aligned}$$

but a quick rewriting of $\tilde{\rho}^{1/3}(\mathbf{r}, t)$ gives us:

$$\begin{aligned}
\tilde{\rho}^{1/3}(\mathbf{r}, t) &= \left(1 + \sum_{LM}^* \tilde{\rho}_{LM} Y_{LM} \right)^{1/3} \\
&= (1 + x)^{1/3}, \quad (C.6)
\end{aligned}$$

which can be calculated using the binomial form¹:

$$\begin{aligned}
\tilde{\rho}^{1/3}(\mathbf{r}, t) &= 1 + \frac{1}{3} \sum_{LM}^* \tilde{\rho}_{LM}(r, t) Y_{LM}(\Omega) \\
&\quad - \frac{1}{9} \sum_{L_1 M_1}^* \sum_{L_2 M_2}^* \tilde{\rho}_{L_1 M_1}(r, t) \tilde{\rho}_{L_2 M_2}(r, t) Y_{L_1 M_1}(\Omega) Y_{L_2 M_2}(\Omega) + \dots \quad (C.7)
\end{aligned}$$

Now we just have a product of spherical harmonics, which we can solve by using (A.6):

$$Y_{l_1 m_1}(\Omega) Y_{l_2 m_2}(\Omega) = \sum_{l=|l_1-l_2|}^{l_1+l_2} \sum_{m=-l}^l \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}} C_{l_1 0 l_2 0}^{l 0} C_{l_1 m_1 l_2 m_2}^{l m} Y_{lm}(\Omega). \quad (A.6)$$

¹note that x is only close to zero if the density in the $L = 0$ orbitals dominate all the other orbitals.

By using the above we get:

$$\begin{aligned}
\tilde{\rho}^{1/3}(\mathbf{r}, t) &= 1 + \frac{1}{3} \sum_{LM}^* \tilde{\rho}_{LM}(r, t) Y_{LM}(\Omega) \\
&\quad - \frac{1}{9} \sum_{L_1 M_1}^* \sum_{L_2 M_2}^* \tilde{\rho}_{L_1 M_1}(r, t) \tilde{\rho}_{L_2 M_2}(r, t) \sum_{l=|l_1-l_2|}^{l_1+l_2} \sum_{m=-l}^l \\
&\quad \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}} C_{l_1 0 l_2 0}^{l 0} C_{l_1 m_1 l_2 m_2}^{l m} Y_{lm}(\Omega) + \dots
\end{aligned} \tag{C.8}$$

Hence $\rho^{1/3}$ can be approximated as:

$$\begin{aligned}
\rho^{1/3}(\mathbf{r}, t) &= \left(\frac{\rho_{00}}{\sqrt{4\pi}} \right)^{1/3} \tilde{\rho}^{1/3}(\mathbf{r}, t) \\
&= \left(\frac{\rho_{00}}{\sqrt{4\pi}} \right)^{1/3} \left(1 + \frac{1}{3} \sum_{LM}^* \tilde{\rho}_{LM}(r, t) Y_{LM}(\Omega) \right. \\
&\quad \left. - \frac{1}{9} \sum_{L_1 M_1}^* \sum_{L_2 M_2}^* \tilde{\rho}_{L_1 M_1}(r, t) \tilde{\rho}_{L_2 M_2}(r, t) \sum_{l=|l_1-l_2|}^{l_1+l_2} \sum_{m=-l}^l \right. \\
&\quad \left. \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}} C_{l_1 0 l_2 0}^{l 0} C_{l_1 m_1 l_2 m_2}^{l m} Y_{lm}(\Omega) + \dots \right)
\end{aligned} \tag{C.9}$$

So this is a third order approximation in the spherical harmonic basis, higher order terms could of course be calculated in the same way.

The good about this method is that now we have calculated an approximation to $\rho^{1/3}$ and need an approximation to $\rho^{4/3}$. This is easily done by using the binomial expansion:

$$(1+x)^{4/3} = 1 + \frac{4}{3}x + \frac{2}{9}x^2 - \frac{4}{81}x^3 + \dots \tag{C.10}$$

hence we see that the powers are the same all we need to do is change the front-factors.

Appendix D

The commutator in Runge-Gross theorem 1

Our starting point is the following commutator which needs to be evaluated:

$$i \frac{\partial}{\partial t} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]_{t=t_0} = \langle \Psi_0 | [\hat{j}(\mathbf{r}), \hat{v}_1(t_0) - \hat{v}_2(t_0)] | \Psi_0 \rangle. \quad (4.9)$$

where the current operator was given in (4.4) as:

$$\hat{j}(\mathbf{r}) = \frac{1}{2i} \sum_{\sigma} \nabla \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) - \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \nabla \hat{\psi}_{\sigma}(\mathbf{r}), \quad (4.4)$$

To keep it as short as possible we only look at one of the external potentials, hence we define I_v :

$$I_v = -i \langle \Psi_0 | [\hat{j}(\mathbf{r}), \hat{v}(t_0)] | \Psi_0 \rangle. \quad (D.1)$$

Now we insert the current operator as given in (4.4):

$$I_v = \frac{1}{2} \sum_{\sigma} \langle \Psi_0 | \left[\left(\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \nabla_r \hat{\psi}_{\sigma}(\mathbf{r}) - \nabla_r \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \right), \hat{v}(t_0) \right] | \Psi_0 \rangle. \quad (D.2)$$

Similarly we convert the external potential operator to the external potential:

$$I_v = \frac{1}{2} \sum_{\sigma} \langle \Psi_0 | \left[\left(\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \nabla_r \hat{\psi}_{\sigma}(\mathbf{r}) - \nabla_r \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \right), \sum_{\sigma'} \int d^3 r' v(\mathbf{r}', t_0) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \right] | \Psi_0 \rangle. \quad (D.3)$$

We expand the commutator:

$$\begin{aligned}
I_v &= \frac{1}{2} \sum_{\sigma\sigma'} \langle \Psi_0 | \\
&\quad \left(\hat{\psi}_\sigma^\dagger(\mathbf{r}) \nabla_r \hat{\psi}_\sigma(\mathbf{r}) - \nabla_r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \right) \int d^3 r' v(\mathbf{r}', t_0) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \\
&\quad - \int d^3 r' v(\mathbf{r}', t_0) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \left(\hat{\psi}_\sigma^\dagger(\mathbf{r}) \nabla_r \hat{\psi}_\sigma(\mathbf{r}) - \nabla_r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \right) | \Psi_0 \rangle \\
&= \frac{1}{2} \sum_{\sigma\sigma'} \int d^3 r' \langle \Psi_0 | v(\mathbf{r}', t_0) \\
&\quad \left\{ \hat{\psi}_\sigma^\dagger(\mathbf{r}) \nabla_r \hat{\psi}_\sigma(\mathbf{r}) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') - \nabla_r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \right. \\
&\quad \left. - \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_\sigma^\dagger(\mathbf{r}) \nabla_r \hat{\psi}_\sigma(\mathbf{r}) + \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \nabla_r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \right\} | \Psi_0 \rangle.
\end{aligned} \tag{D.4}$$

So now we have four terms. The evaluation of the different terms and the rest of this calculation is done in momentum space. The conversion between field operators and momentum space is given as:

$$\begin{aligned}
\hat{\psi}_\sigma^\dagger(\mathbf{r}) &= \sum_k \hat{a}_{k\sigma}^\dagger \psi_{k\sigma}(\mathbf{r}) \\
\hat{\psi}_\sigma(\mathbf{r}) &= \sum_k \hat{a}_{k\sigma} \psi_{k\sigma}(\mathbf{r}).
\end{aligned} \tag{D.5}$$

The relevant part of (D.4) when commuting is:

$$I_1 = \hat{\psi}_\sigma^\dagger(\mathbf{r}) \nabla_r \hat{\psi}_\sigma(\mathbf{r}) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \tag{D.6}$$

By converting the field operators to momentum space we get:

$$\begin{aligned}
I_1 &= \sum_{k_1} \hat{a}_{k_1\sigma}^\dagger \psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \left(\sum_{k_2} \hat{a}_{k_2\sigma} \psi_{k_2\sigma}(\mathbf{r}) \right) \sum_{k_3} \hat{a}_{k_3\sigma'}^\dagger \psi_{k_3\sigma'}^*(\mathbf{r}') \sum_{k_4} \hat{a}_{k_4\sigma'} \psi_{k_4\sigma'}(\mathbf{r}') \\
&= \sum_{k_1 k_2 k_3 k_4} \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_2\sigma} \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_4\sigma'} \psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) \psi_{k_3\sigma'}^*(\mathbf{r}') \psi_{k_4\sigma'}(\mathbf{r}').
\end{aligned} \tag{D.7}$$

In the same fashion we make the second term:

$$\begin{aligned}
I_2 &= -\nabla_r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \\
&= -\sum_{k_1 k_2 k_3 k_4} \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_2\sigma} \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_4\sigma'} \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r}) \psi_{k_3\sigma'}^*(\mathbf{r}') \psi_{k_4\sigma'}(\mathbf{r}').
\end{aligned} \tag{D.8}$$

and the third term:

$$\begin{aligned}
I_3 &= -\hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_\sigma^\dagger(\mathbf{r}) \nabla_r \hat{\psi}_\sigma(\mathbf{r}) \\
&= -\sum_{k_1 k_2 k_3 k_4} \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_4\sigma'} \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_2\sigma} \psi_{k_3\sigma'}^*(\mathbf{r}') \psi_{k_4\sigma'}(\mathbf{r}') \psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}).
\end{aligned} \tag{D.9}$$

and the fourth and final term:

$$\begin{aligned} I_4 &= \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \hat{\psi}_{\sigma'}(\mathbf{r}') \nabla_r \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \\ &= \sum_{k_1 k_2 k_3 k_4} \hat{a}_{k_3 \sigma'}^{\dagger} \hat{a}_{k_4 \sigma'} \hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_2 \sigma} \psi_{k_3 \sigma}^*(\mathbf{r}') \psi_{k_4 \sigma}(\mathbf{r}') \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \psi_{k_2 \sigma}(\mathbf{r}). \end{aligned} \quad (\text{D.10})$$

By combining all the terms we get:

$$\begin{aligned} I &= I_1 + I_2 + I_3 + I_4 \\ &= \sum_{k_1 k_2 k_3 k_4} \left[\hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_2 \sigma} \hat{a}_{k_3 \sigma'}^{\dagger} \hat{a}_{k_4 \sigma'} - \hat{a}_{k_3 \sigma'}^{\dagger} \hat{a}_{k_4 \sigma'} \hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_2 \sigma} \right] \psi_{k_3 \sigma}^*(\mathbf{r}') \psi_{k_4 \sigma}(\mathbf{r}') \\ &\quad \left[\psi_{k_1 \sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2 \sigma}(\mathbf{r}) - \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \psi_{k_2 \sigma}(\mathbf{r}) \right]. \end{aligned} \quad (\text{D.11})$$

The idea is now to commute the order of the creation and annihilation operators in the second term to look like the first term.

So far we have said nothing about whether these particles are fermions or bosons. The reason why we have not mentioned this is because even though they fulfil different commutation relations they end up giving the same in the end.

Let us show that.

Fermions fulfil the anti-commutator relations:

$$\begin{aligned} \{ \hat{a}_{k_i \sigma}^{\dagger}, \hat{a}_{k_j \sigma'} \} &= \delta_{\sigma \sigma'} \delta_{k_i k_j} \\ \{ \hat{a}_{k_i \sigma}, \hat{a}_{k_j \sigma'} \} &= 0, \end{aligned} \quad (\text{D.12})$$

where the anti commutator is given as:

$$\{A, B\} = AB + BA. \quad (\text{D.13})$$

If we assume our system consists of fermions we can reorder the operators as follows:

$$\begin{aligned} \hat{a}_{k_3 \sigma'}^{\dagger} \hat{a}_{k_4 \sigma'} \hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_2 \sigma} &= \hat{a}_{k_3 \sigma'}^{\dagger} \left(\delta_{\sigma \sigma'} \delta_{k_4 k_1} - \hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_4 \sigma'} \right) \hat{a}_{k_2 \sigma} \\ &= \hat{a}_{k_3 \sigma'}^{\dagger} \delta_{\sigma \sigma'} \delta_{k_4 k_1} \hat{a}_{k_2 \sigma} - \hat{a}_{k_3 \sigma'}^{\dagger} \hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_4 \sigma'} \hat{a}_{k_2 \sigma} \\ &= \hat{a}_{k_3 \sigma'}^{\dagger} \delta_{\sigma \sigma'} \delta_{k_4 k_1} \hat{a}_{k_2 \sigma} + \hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_3 \sigma'}^{\dagger} \hat{a}_{k_4 \sigma'} \hat{a}_{k_2 \sigma} \\ &= \hat{a}_{k_3 \sigma'}^{\dagger} \delta_{\sigma \sigma'} \delta_{k_4 k_1} \hat{a}_{k_2 \sigma} - \hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_3 \sigma'}^{\dagger} \hat{a}_{k_2 \sigma} \hat{a}_{k_4 \sigma'} \\ &= \hat{a}_{k_3 \sigma'}^{\dagger} \delta_{\sigma \sigma'} \delta_{k_4 k_1} \hat{a}_{k_2 \sigma} - \hat{a}_{k_1 \sigma}^{\dagger} \left(\delta_{\sigma \sigma'} \delta_{k_3 k_2} - \hat{a}_{k_2 \sigma} \hat{a}_{k_3 \sigma'}^{\dagger} \right) \hat{a}_{k_4 \sigma'} \\ &= \hat{a}_{k_3 \sigma'}^{\dagger} \delta_{\sigma \sigma'} \delta_{k_4 k_1} \hat{a}_{k_2 \sigma} - \hat{a}_{k_1 \sigma}^{\dagger} \delta_{\sigma \sigma'} \delta_{k_3 k_2} \hat{a}_{k_4 \sigma'} \\ &\quad + \hat{a}_{k_1 \sigma}^{\dagger} \hat{a}_{k_2 \sigma} \hat{a}_{k_3 \sigma'}^{\dagger} \hat{a}_{k_4 \sigma'}, \end{aligned} \quad (\text{D.14})$$

which we can insert directly into (D.11), but before we make the same calculation for bosons.

Bosons fulfil the commutator relations:

$$\begin{aligned} \left[\hat{a}_{k_i\sigma}, \hat{a}_{k_j\sigma'}^\dagger \right] &= \delta_{\sigma\sigma'} \delta_{k_i k_j} \\ \left[\hat{a}_{k_i\sigma}, \hat{a}_{k_j\sigma'} \right] &= 0, \end{aligned} \quad (\text{D.15})$$

where the commutator is given as:

$$[A, B] = AB - BA. \quad (\text{D.16})$$

If we assume our system consists of bosons we can reorder the operators as follows:

$$\begin{aligned} \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_4\sigma'} \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_2\sigma} &= \hat{a}_{k_3\sigma'}^\dagger \left(\delta_{\sigma\sigma'} \delta_{k_4 k_1} + \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_4\sigma'} \right) \hat{a}_{k_2\sigma} \\ &= \hat{a}_{k_3\sigma'}^\dagger \delta_{\sigma\sigma'} \delta_{k_4 k_1} \hat{a}_{k_2\sigma} + \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_4\sigma'} \hat{a}_{k_2\sigma} \\ &= \hat{a}_{k_3\sigma'}^\dagger \delta_{\sigma\sigma'} \delta_{k_4 k_1} \hat{a}_{k_2\sigma} + \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_4\sigma'} \hat{a}_{k_2\sigma} \\ &= \hat{a}_{k_3\sigma'}^\dagger \delta_{\sigma\sigma'} \delta_{k_4 k_1} \hat{a}_{k_2\sigma} + \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_2\sigma} \hat{a}_{k_4\sigma'} \\ &= \hat{a}_{k_3\sigma'}^\dagger \delta_{\sigma\sigma'} \delta_{k_4 k_1} \hat{a}_{k_2\sigma} + \hat{a}_{k_1\sigma}^\dagger \left(-\delta_{\sigma\sigma'} \delta_{k_3 k_2} + \hat{a}_{k_2\sigma} \hat{a}_{k_3\sigma'}^\dagger \right) \hat{a}_{k_4\sigma'} \\ &= \hat{a}_{k_3\sigma'}^\dagger \delta_{\sigma\sigma'} \delta_{k_4 k_1} \hat{a}_{k_2\sigma} - \hat{a}_{k_1\sigma}^\dagger \delta_{\sigma\sigma'} \delta_{k_3 k_2} \hat{a}_{k_4\sigma'} \\ &\quad + \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_2\sigma} \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_4\sigma'}, \end{aligned} \quad (\text{D.17})$$

and we see the end result of the reordering is exactly the same as for fermions. Hence in the following when we insert the reordered operators into (D.11) no limitation on the type of particles involved is needed.

We insert the reordering done in (D.14)/(D.17) into (D.11) and get:

$$\begin{aligned} I &= \sum_{k_1 k_2 k_3 k_4} \left[\hat{a}_{k_1\sigma}^\dagger \delta_{\sigma\sigma'} \delta_{k_3 k_2} \hat{a}_{k_4\sigma'} - \hat{a}_{k_3\sigma'}^\dagger \delta_{\sigma\sigma'} \delta_{k_4 k_1} \hat{a}_{k_2\sigma} \right] \\ &\quad \psi_{k_3\sigma'}^*(\mathbf{r}') \psi_{k_4\sigma}(\mathbf{r}') \left[\psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) - \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r}) \right]. \end{aligned} \quad (\text{D.18})$$

We split the expression in two terms and use the delta-function to remove one sum in each:

$$\begin{aligned} I &= \delta_{\sigma\sigma'} \sum_{k_1 k_2 k_4} \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_4\sigma'} \psi_{k_2\sigma}^*(\mathbf{r}') \psi_{k_4\sigma}(\mathbf{r}') \left[\psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) - \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r}) \right] \\ &\quad - \delta_{\sigma\sigma'} \sum_{k_1 k_2 k_3} \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_2\sigma} \psi_{k_3\sigma}^*(\mathbf{r}') \psi_{k_1\sigma}(\mathbf{r}') \left[\psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) - \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r}) \right] \end{aligned} \quad (\text{D.19})$$

In the first term we rename k_4 to k_3 which enables us to contract the terms again:

$$\begin{aligned}
I &= \delta_{\sigma\sigma'} \sum_{k_1 k_2 k_3} \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_3\sigma'} \psi_{k_2\sigma}^*(\mathbf{r}') \psi_{k_3\sigma}(\mathbf{r}') [\psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) - \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r})] \\
&\quad - \delta_{\sigma\sigma'} \sum_{k_1 k_2 k_3} \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_2\sigma} \psi_{k_3\sigma}^*(\mathbf{r}') \psi_{k_1\sigma}(\mathbf{r}') [\psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) - \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r})] \\
&= \delta_{\sigma\sigma'} \sum_{k_1 k_2 k_3} \left[\hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_3\sigma'} \psi_{k_2\sigma}^*(\mathbf{r}') \psi_{k_3\sigma}(\mathbf{r}') - \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_2\sigma} \psi_{k_3\sigma}^*(\mathbf{r}') \psi_{k_1\sigma}(\mathbf{r}') \right] \\
&\quad [\psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) - \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r})].
\end{aligned} \tag{D.20}$$

Finally we insert (D.20) into our original expression which was given in (D.4):

$$\begin{aligned}
I_v &= \frac{1}{2} \sum_{\sigma\sigma'} \int d^3 r' \langle \Psi_0 | v(\mathbf{r}', t_0) \delta_{\sigma\sigma'} \sum_{k_1 k_2 k_3} \\
&\quad \left[\hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_3\sigma'} \psi_{k_2\sigma}^*(\mathbf{r}') \psi_{k_3\sigma}(\mathbf{r}') - \hat{a}_{k_3\sigma'}^\dagger \hat{a}_{k_2\sigma} \psi_{k_3\sigma}^*(\mathbf{r}') \psi_{k_1\sigma}(\mathbf{r}') \right] \\
&\quad [\psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) - \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r})] | \Psi_0 \rangle.
\end{aligned} \tag{D.21}$$

By using the delta-function we remove one of the spin sums, and after a reordering of the terms we get:

$$\begin{aligned}
I_v &= \frac{1}{2} \sum_{\sigma, k_1 k_2 k_3} \int d^3 r' v(\mathbf{r}', t_0) \langle \Psi_0 | \\
&\quad \left[\hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_3\sigma} \psi_{k_2\sigma}^*(\mathbf{r}') \psi_{k_3\sigma}(\mathbf{r}') - \hat{a}_{k_3\sigma}^\dagger \hat{a}_{k_2\sigma} \psi_{k_3\sigma}^*(\mathbf{r}') \psi_{k_1\sigma}(\mathbf{r}') \right] \\
&\quad [\psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) - \nabla_r \psi_{k_1\sigma}^*(\mathbf{r}) \psi_{k_2\sigma}(\mathbf{r})] | \Psi_0 \rangle,
\end{aligned} \tag{D.22}$$

again we see that we have four terms. Each of these four terms needs to be evaluated. I_v is split in the four terms:

$$I_v = \tilde{I}_{11} + \tilde{I}_{12} + \tilde{I}_{21} + \tilde{I}_{22} \tag{D.23}$$

where \tilde{I}_{ij} is the i 'th term in the first bracket, multiplied by the j 'th term in the second bracket.

The first term \tilde{I}_{11} is given as:

$$\begin{aligned}
I_v &= \frac{1}{2} \sum_{\sigma, k_1 k_2 k_3} \int d^3 r' v(\mathbf{r}', t_0) \langle \Psi_0 | \\
&\quad \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_3\sigma} \psi_{k_2\sigma}^*(\mathbf{r}') \psi_{k_3\sigma}(\mathbf{r}') \psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) | \Psi_0 \rangle.
\end{aligned} \tag{D.24}$$

We reorder the expression:

$$\begin{aligned}
\tilde{I}_{11} &= \frac{1}{2} \sum_{\sigma, k_1 k_2 k_3} \int d^3 r' v(\mathbf{r}', t_0) \psi_{k_2\sigma}^*(\mathbf{r}') \psi_{k_3\sigma}(\mathbf{r}') \psi_{k_1\sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2\sigma}(\mathbf{r}) \\
&\quad \langle \Psi_0 | \hat{a}_{k_1\sigma}^\dagger \hat{a}_{k_3\sigma} | \Psi_0 \rangle.
\end{aligned} \tag{D.25}$$

The gradient ignores terms which does not depend on r , we use this to include another term under the gradient:

$$\begin{aligned} \tilde{I}_{11} = & \frac{1}{2} \sum_{\sigma, k_1 k_2 k_3} \int d^3 r' v(\mathbf{r}', t_0) \psi_{k_3 \sigma}(\mathbf{r}') \psi_{k_1 \sigma}^*(\mathbf{r}) \nabla_r (\psi_{k_2 \sigma}^*(\mathbf{r}') \psi_{k_2 \sigma}(\mathbf{r})) \\ & \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle. \end{aligned} \quad (\text{D.26})$$

Next we use the completeness of the wavefunctions:

$$\delta(\mathbf{r} - \mathbf{r}') = \sum_k \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}'), \quad (\text{D.51})$$

which is derived at the end of this section on page 109. By using (D.51) on (D.26) we get:

$$\begin{aligned} \tilde{I}_{11} = & \frac{1}{2} \sum_{\sigma, k_1 k_3} \int d^3 r' v(\mathbf{r}', t_0) \psi_{k_3 \sigma}(\mathbf{r}') \psi_{k_1 \sigma}^*(\mathbf{r}) \nabla_r \delta(\mathbf{r} - \mathbf{r}') \\ & \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle. \end{aligned} \quad (\text{D.27})$$

next we use another delta-function relation which is also derived at the end of this section on page 110:

$$\nabla_r \delta(\mathbf{r} - \mathbf{r}') = -\nabla_{r'} \delta(\mathbf{r} - \mathbf{r}'). \quad (\text{D.54})$$

We use (D.54) on (D.27) to change the coordinate of the gradient:

$$\begin{aligned} \tilde{I}_{11} = & -\frac{1}{2} \sum_{\sigma, k_1 k_3} \int d^3 r' v(\mathbf{r}', t_0) \psi_{k_3 \sigma}(\mathbf{r}') \psi_{k_1 \sigma}^*(\mathbf{r}) \nabla_{r'} \delta(\mathbf{r} - \mathbf{r}') \\ & \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle. \end{aligned} \quad (\text{D.28})$$

We now make a partial integration which shift the gradient from the delta function to the wavefunction and external potential, at the cost of a surface term:

$$\begin{aligned} \tilde{I}_{11} = & -\frac{1}{2} \sum_{\sigma, k_1 k_3} v(\mathbf{r}', t_0) \psi_{k_3 \sigma}(\mathbf{r}') \psi_{k_1 \sigma}^*(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle \Big|_{r'=-\infty}^{r'=\infty} \\ & + \frac{1}{2} \sum_{\sigma, k_1 k_3} \int d^3 r' \nabla_{r'} [v(\mathbf{r}', t_0) \psi_{k_3 \sigma}(\mathbf{r}')] \psi_{k_1 \sigma}^*(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle. \end{aligned} \quad (\text{D.29})$$

The first term is zero for any finite system. In the second term we use the delta-function to remove the integral and let the gradient work according to the product rule for differentiation:

$$\begin{aligned} \tilde{I}_{11} = & \frac{1}{2} \sum_{\sigma, k_1 k_3} [\nabla_r v(\mathbf{r}, t_0) \psi_{k_3 \sigma}(\mathbf{r}) + v(\mathbf{r}, t_0) \nabla_r \psi_{k_3 \sigma}(\mathbf{r})] \psi_{k_1 \sigma}^*(\mathbf{r}) \\ & \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle. \end{aligned} \quad (\text{D.30})$$

We split the terms:

$$\begin{aligned}\tilde{I}_{11} &= \frac{1}{2} \sum_{\sigma, k_1 k_3} \nabla_r v(\mathbf{r}, t_0) \psi_{k_3 \sigma}(\mathbf{r}) \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle \\ &+ \frac{1}{2} \sum_{\sigma, k_1 k_3} v(\mathbf{r}, t_0) \nabla_r \psi_{k_3 \sigma}(\mathbf{r}) \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle.\end{aligned}\quad (\text{D.31})$$

In the first term we convert the number operators back to field operators:

$$\begin{aligned}\tilde{I}_{11} &= \frac{1}{2} \sum_{\sigma} \nabla_r v(\mathbf{r}, t_0) \langle \Psi_0 | \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) | \Psi_0 \rangle \\ &+ \frac{1}{2} \sum_{\sigma, k_1 k_3} v(\mathbf{r}, t_0) \nabla_r \psi_{k_3 \sigma}(\mathbf{r}) \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle.\end{aligned}\quad (\text{D.32})$$

In the first term we use the fact that the field operators in the bracket is the density operator:

$$\begin{aligned}\tilde{I}_{11} &= \frac{1}{2} \sum_{\sigma} \nabla_r v(\mathbf{r}, t_0) \langle \Psi_0 | \hat{\rho}_{\sigma}(\mathbf{r}) | \Psi_0 \rangle \\ &+ \frac{1}{2} \sum_{\sigma, k_1 k_3} v(\mathbf{r}, t_0) \nabla_r \psi_{k_3 \sigma}(\mathbf{r}) \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle.\end{aligned}\quad (\text{D.33})$$

In the first term the density operator bracket is turned into the density, in the second term we change k_3 to k_2 :

$$\begin{aligned}\tilde{I}_{11} &= \frac{1}{2} \nabla_r v(\mathbf{r}, t_0) \rho(\mathbf{r}, t_0) \\ &+ \frac{1}{2} \sum_{\sigma, k_1 k_2} v(\mathbf{r}, t_0) \nabla_r \psi_{k_2 \sigma}(\mathbf{r}) \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_2 \sigma} | \Psi_0 \rangle.\end{aligned}\quad (\text{D.34})$$

the second term \tilde{I}_{12} is given as:

$$\begin{aligned}\tilde{I}_{12} &= -\frac{1}{2} \sum_{\sigma, k_1 k_2 k_3} \int d^3 r' v(\mathbf{r}', t_0) \\ &\langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} \psi_{k_2 \sigma}^*(\mathbf{r}') \psi_{k_3 \sigma}(\mathbf{r}') \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \psi_{k_2 \sigma}(\mathbf{r}) | \Psi_0 \rangle.\end{aligned}\quad (\text{D.35})$$

We reorder the expression:

$$\begin{aligned}\tilde{I}_{12} &= -\frac{1}{2} \sum_{\sigma, k_1 k_2 k_3} \int d^3 r' v(\mathbf{r}', t_0) \psi_{k_3 \sigma}(\mathbf{r}') \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \psi_{k_2 \sigma}^*(\mathbf{r}') \psi_{k_2 \sigma}(\mathbf{r}) \\ &\langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle,\end{aligned}\quad (\text{D.36})$$

and use the completeness relation given in (D.51):

$$\begin{aligned} \tilde{I}_{12} = & -\frac{1}{2} \sum_{\sigma, k_1 k_3} \int d^3 r' v(\mathbf{r}', t_0) \psi_{k_3 \sigma}(\mathbf{r}') \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \\ & \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle. \end{aligned} \quad (\text{D.37})$$

The delta-function lifts the integral:

$$\tilde{I}_{12} = -\frac{1}{2} \sum_{\sigma, k_1 k_3} v(\mathbf{r}, t_0) \psi_{k_3 \sigma}(\mathbf{r}) \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_3 \sigma} | \Psi_0 \rangle, \quad (\text{D.38})$$

and finally we change k_3 to k_2 :

$$\tilde{I}_{12} = -\frac{1}{2} \sum_{\sigma, k_1 k_2} v(\mathbf{r}, t_0) \psi_{k_2 \sigma}(\mathbf{r}) \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_2 \sigma} | \Psi_0 \rangle. \quad (\text{D.39})$$

the third term, \tilde{I}_{21} , is given as:

$$\begin{aligned} \tilde{I}_{21} = & -\frac{1}{2} \sum_{\sigma, k_1 k_2 k_3} \int d^3 r' v(\mathbf{r}', t_0) \\ & \langle \Psi_0 | \hat{a}_{k_3 \sigma}^\dagger \hat{a}_{k_2 \sigma} \psi_{k_3 \sigma}^*(\mathbf{r}') \psi_{k_1 \sigma}(\mathbf{r}') \psi_{k_1 \sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2 \sigma}(\mathbf{r}) | \Psi_0 \rangle. \end{aligned} \quad (\text{D.40})$$

The procedure for manipulating this expression is completely similar to the one used in the second term, hence we skip the actual calculation and give the end result, which is:

$$\tilde{I}_{21} = \frac{1}{2} \sum_{\sigma, k_1 k_2} v(\mathbf{r}, t_0) \psi_{k_1 \sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2 \sigma}(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_2 \sigma} | \Psi_0 \rangle. \quad (\text{D.41})$$

The fourth term, \tilde{I}_{22} , is given as:

$$\begin{aligned} \tilde{I}_{22} = & \frac{1}{2} \sum_{\sigma, k_1 k_2 k_3} \int d^3 r' v(\mathbf{r}', t_0) \\ & \langle \Psi_0 | \hat{a}_{k_3 \sigma}^\dagger \hat{a}_{k_2 \sigma} \psi_{k_3 \sigma}^*(\mathbf{r}') \psi_{k_1 \sigma}(\mathbf{r}') \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \psi_{k_2 \sigma}(\mathbf{r}) | \Psi_0 \rangle. \end{aligned} \quad (\text{D.42})$$

The procedure for manipulating this expression is completely similar to the one used in the first term, hence we skip the actual calculation and give the end result, which is:

$$\begin{aligned} \tilde{I}_{22} = & \frac{1}{2} \nabla_r v(\mathbf{r}, t_0) \rho(\mathbf{r}, t_0) \\ & + \frac{1}{2} \sum_{\sigma, k_1 k_2} v(\mathbf{r}, t_0) \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \psi_{k_2 \sigma}(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_2 \sigma} | \Psi_0 \rangle. \end{aligned} \quad (\text{D.43})$$

So the four terms are:

$$\begin{aligned} \tilde{I}_{11} &= \frac{1}{2} \nabla_r v(\mathbf{r}, t_0) \rho(\mathbf{r}, t_0) \\ &+ \frac{1}{2} \sum_{\sigma, k_1 k_2} v(\mathbf{r}, t_0) \nabla_r \psi_{k_2 \sigma}(\mathbf{r}) \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_2 \sigma} | \Psi_0 \rangle \end{aligned} \quad (\text{D.44})$$

$$\tilde{I}_{12} = -\frac{1}{2} \sum_{\sigma, k_1 k_2} v(\mathbf{r}, t_0) \psi_{k_2 \sigma}(\mathbf{r}) \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_2 \sigma} | \Psi_0 \rangle \quad (\text{D.45})$$

$$\tilde{I}_{21} = -\frac{1}{2} \sum_{\sigma, k_1 k_2} v(\mathbf{r}, t_0) \psi_{k_1 \sigma}^*(\mathbf{r}) \nabla_r \psi_{k_2 \sigma}(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_2 \sigma} | \Psi_0 \rangle \quad (\text{D.46})$$

$$\begin{aligned} \tilde{I}_{22} &= \frac{1}{2} \nabla_r v(\mathbf{r}, t_0) \rho(\mathbf{r}, t_0) \\ &+ \frac{1}{2} \sum_{\sigma, k_1 k_2} v(\mathbf{r}, t_0) \nabla_r \psi_{k_1 \sigma}^*(\mathbf{r}) \psi_{k_2 \sigma}(\mathbf{r}) \langle \Psi_0 | \hat{a}_{k_1 \sigma}^\dagger \hat{a}_{k_2 \sigma} | \Psi_0 \rangle. \end{aligned} \quad (\text{D.47})$$

By summing the terms we get:

$$\begin{aligned} I_v &= \tilde{I}_{11} + \tilde{I}_{12} + \tilde{I}_{21} + \tilde{I}_{22} \\ &= \nabla_r v(\mathbf{r}, t_0) \rho(\mathbf{r}, t_0). \end{aligned} \quad (\text{D.48})$$

We insert this into our original expression for I_v given in (D.1), which gives us:

$$-i \langle \Psi_0 | [\hat{j}(\mathbf{r}), \hat{v}(t_0)] | \Psi_0 \rangle = \nabla_r v(\mathbf{r}, t_0) \rho(\mathbf{r}, t_0). \quad (\text{D.49})$$

from this we find that the expression which we seek can be written as:

$$\frac{\partial}{\partial t} [j_1(\mathbf{r}, t) - j_2(\mathbf{r}, t)]_{t=t_0} = \nabla_r [v_1(\mathbf{r}, t_0) - v_2(\mathbf{r}, t_0)] \rho(\mathbf{r}, t_0). \quad (\text{D.50})$$

two delta-function properties which we used

completeness relation We show that a delta-function can be written as:

$$\delta(\mathbf{r} - \mathbf{r}') = \sum_k \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}'), \quad (\text{D.51})$$

independently of whether we are dealing with fermions or bosons.

For fermions we have:

$$\begin{aligned}
\delta(\mathbf{r} - \mathbf{r}') &= \{\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}(\mathbf{r}')\} \\
&= \sum_{kk'} \{\hat{a}_k^\dagger \psi_k^*(\mathbf{r}), \hat{a}_{k'} \psi_{k'}(\mathbf{r}')\} \\
&= \sum_{kk'} \psi_k^*(\mathbf{r}) \psi_{k'}(\mathbf{r}') \{\hat{a}_k^\dagger, \hat{a}_{k'}\} \\
&= \sum_{kk'} \psi_k^*(\mathbf{r}) \psi_{k'}(\mathbf{r}') \delta_{kk'} \\
&= \sum_k \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}').
\end{aligned} \tag{D.52}$$

For bosons we have:

$$\begin{aligned}
\delta(\mathbf{r} - \mathbf{r}') &= [\hat{\psi}^\dagger(\mathbf{r}), \hat{\psi}(\mathbf{r}')] \\
&= \sum_{kk'} [\hat{a}_k^\dagger \psi_k^*(\mathbf{r}), \hat{a}_{k'} \psi_{k'}(\mathbf{r}')] \\
&= \sum_{kk'} \psi_k^*(\mathbf{r}) \psi_{k'}(\mathbf{r}') [\hat{a}_k^\dagger, \hat{a}_{k'}] \\
&= \sum_{kk'} \psi_k^*(\mathbf{r}) \psi_{k'}(\mathbf{r}') \delta_{kk'} \\
&= \sum_k \psi_k^*(\mathbf{r}) \psi_k(\mathbf{r}').
\end{aligned} \tag{D.53}$$

Hence we have shown that equation (D.51) is valid for both bosons and fermions.

Coordinate shift in gradient delta-functions We show that a coordinate shift in the gradient working on a delta-function gives a sign shift:

$$\nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') = -\nabla_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') \tag{D.54}$$

One way to show this is by using the Fouriertransform of the delta-function[40, p. 938]:

$$\delta(\mathbf{r} - \mathbf{r}') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega(\mathbf{r}-\mathbf{r}')} \tag{D.55}$$

We see now that the gradient with regard to coordinate r gives:

$$\begin{aligned}
\nabla_{\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') &= \nabla_{\mathbf{r}} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega(\mathbf{r}-\mathbf{r}')} \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega i\omega e^{i\omega(\mathbf{r}-\mathbf{r}')}
\end{aligned} \tag{D.56}$$

whereas the gradient with regard to coordinate r' gives:

$$\begin{aligned}
\nabla_{\mathbf{r}'} \delta(\mathbf{r} - \mathbf{r}') &= \nabla_{\mathbf{r}'} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega(\mathbf{r}-\mathbf{r}')} \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega (-i\omega) e^{i\omega(\mathbf{r}-\mathbf{r}')}
\end{aligned} \tag{D.57}$$

By comparing (D.56) and (D.57) we get the desired expression:

$$\nabla_{\mathbf{r}}\delta(\mathbf{r} - \mathbf{r}') = -\nabla_{\mathbf{r}'}\delta(\mathbf{r} - \mathbf{r}') \quad (\text{D.58})$$

Appendix E

Showing $\langle u_{x,i\sigma} \rangle_{i\sigma} = \langle u_{x,i\sigma}^* \rangle_{i\sigma}$

This appendix is tied to chapter 3. We seek to show the following relation:

$$\langle u_{x,i\sigma} \rangle_{i\sigma} = \langle u_{x,i\sigma}^* \rangle_{i\sigma} \quad (\text{E.1})$$

which is need in order to get equation (3.66).

By insertion we rewrite the left side as:

$$\begin{aligned} \langle u_{x,i\sigma} \rangle_{i\sigma} &= \int d\mathbf{r} \psi_{i\sigma}^*(\mathbf{r}) u_{x,i\sigma}(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}) \\ &= \int d\mathbf{r} \psi_{i\sigma}^*(\mathbf{r}) \frac{1}{\psi_{i\sigma}^*(\mathbf{r})} \frac{\delta E_x[\psi]}{\delta \psi_{i\sigma}(\mathbf{r})} \psi_{i\sigma}(\mathbf{r}) \\ &= \int d\mathbf{r} \frac{\delta E_x[\psi]}{\delta \psi_{i\sigma}(\mathbf{r})} \psi_{i\sigma}(\mathbf{r}) \end{aligned} \quad (\text{E.2})$$

And the right as:

$$\langle u_{x,i\sigma}^* \rangle_{i\sigma} = \int d\mathbf{r} \frac{\delta E_x[\psi]}{\delta \psi_{i\sigma}^*(\mathbf{r})} \psi_{i\sigma}^*(\mathbf{r}) \quad (\text{E.3})$$

So to reformulate we now need to show the following:

$$\int d\mathbf{r} \frac{\delta E_x[\psi]}{\delta \psi_{i\sigma}(\mathbf{r})} \psi_{i\sigma}(\mathbf{r}) = \int d\mathbf{r} \frac{\delta E_x[\psi]}{\delta \psi_{i\sigma}^*(\mathbf{r})} \psi_{i\sigma}^*(\mathbf{r}) \quad (\text{E.4})$$

Lets take a look at the left hand side:

$$\begin{aligned} \int d\mathbf{r} \frac{\delta E_x[\psi]}{\delta \psi_{i\sigma}(\mathbf{r})} \psi_{i\sigma}(\mathbf{r}) &= - \int d\mathbf{r} \sum_j \psi_{j\sigma}^*(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_{i\sigma}^*(\mathbf{r}') \psi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \psi_{i\sigma}(\mathbf{r}) \\ &= - \int d\mathbf{r} \sum_j \psi_{j\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_{i\sigma}^*(\mathbf{r}') \psi_{j\sigma}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \end{aligned} \quad (\text{E.5})$$

Lets see if we can get the same with the right hand side:

$$\begin{aligned}
\int d\mathbf{r} \frac{\delta E_x[\psi]}{\delta \psi_{i\sigma}^*(\mathbf{r})} \psi_{i\sigma}^*(\mathbf{r}) &= - \int d\mathbf{r} \sum_j \psi_{j\sigma}(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_{j\sigma}^*(\mathbf{r}') \psi_{i\sigma}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \psi_{i\sigma}^*(\mathbf{r}) \\
&= - \int d\mathbf{r} \sum_j \psi_{i\sigma}^*(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_{j\sigma}^*(\mathbf{r}') \psi_{i\sigma}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \\
&= - \int d\mathbf{r}' \sum_j \psi_{j\sigma}^*(\mathbf{r}') \psi_{i\sigma}(\mathbf{r}') \int d\mathbf{r} \frac{\psi_{i\sigma}^*(\mathbf{r}) \psi_{j\sigma}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|} \\
&= - \int d\mathbf{r} \sum_j \psi_{j\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_{i\sigma}^*(\mathbf{r}') \psi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\end{aligned} \tag{E.6}$$

in the last line we switched r and r' around. We now see that the two expressions are the same.

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