universität wien

MASTERARBEIT / MASTER'S THESIS

Titel der Masterarbeit / Title of the Master's Thesis

„Finite Size Corrections in the RPA“

verfasst von / submitted by

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angestrebter akademischer Grad / in partial fulfilment of the requirements for the degree of

Master of Science (MSc)

Wien, 2018

Studienkennzahl lt. Studienblatt / degree programme code as it appears on the student record sheet:	A 066 876
Studienrichtung lt. Studienblatt / degree programme as it appears on the student record sheet:	Masterstudium Physik
Betreut von / Supervisor:	Univ.-Prof. Dipl.-Ing. Dr. Georg Kresse

1 Abstract

A significant challenge of density functional theory (DFT) lies in the approximation of the correlation energy. The so called random phase approximation (RPA) provides an analytical expression for the correlation energy by using the adiabatic connection fluctuation dissipation theorem (ACFDT), a procedure which is implemented in the Vienna ab initio Simulation Package (VASP). Within the RPA, the correlation energy depends on the electronic structure factor of the system. The k-point sampling of the Brillouin zone performed by VASP determines the set of vectors for which the structure factor will be computed. In this thesis, tricubic spline interpolation of the structure factor will be used in order to avoid the computational effort that comes with refining the k-point sampling of the Brillouin zone. The convergence of the correlation energy will then be investigated for a variety of materials including both insulators and semiconductors. We find that the interpolation improves the convergence of the correlation energy for both classes of materials, though in particular for insulators.

2 Zusammenfassung

Das maßgebliche Problem der Dichtefunktionaltheorie (DFT) ist die möglichst genaue Näherung der Korrelationsenergie. In der sogenannten Random Phase Approximation (RPA) wird für diese Energie ein analytischer Ausdruck hergeleitet, indem das Adiabatic Connection Fluctuation Dissipation Theorem (ACFDT) verwendet wird. Diese Methode ist bereits im Vienna ab initio SImulation Package (VASP) implementiert. In der RPA hängt die Korrelationsenergie vom elektronischen Strukturfaktor des Systems ab. Das k-point sampling der Brillouinzone bestimmt die Anzahl der Vektoren, an der der Strukturfaktor von VASP berechnet wird. In dieser Masterarbeit soll eine trikubische Spline Interpolation des Strukturfaktors durchgeführt werden um den rechnerischen Zeitaufwand eines verfeinerten Samplings zu umgehen. Die Konvergenz der Korrelationsenergie, die aus dem interpolierten Strukturfaktor gewonnen wird, soll dann sowohl für Insulatoren als auch für Halbleiter getestet werden. Es zeigt sich, dass die Interpolation die Konvergenz der Korrelationsenergie für beide Klassen von Materialen verbessert, insbesondere jedoch für Insulatoren.

Contents

3 Introduction

The need for novel materials in the industry to fulfill specialized tasks is always increasing. For example, the electronic industry always aims at producing smaller, faster and more efficient processors for computers. To conform to these requirements, detailed knowledge of the materials used for these devices is essential. This is done by performing various experiments on the materials in question. However, this traditional method of conducting research has a few limitations. First, in an experimental setup it is usually not possible to test more than one material at the same time. Additionally, it is hard to maintain extreme outside conditions such as high pressure or high temperature.

In computational materials physics, computer simulations are used to model materials at the quantum mechanical level. The methods used in these simulations have their foundations in theoretical solid state physics. Using computer simulations bears the advantage that the investigation of a large number of materials can be performed a lot faster than in an experimental setup. Also, outside conditions can be implemented very efficiently in modern computer simulations.

In order to perform simulations of materials at the quantum mechanical level, the fundamental equation of quantum mechanics, the many body Schrödinger equation has to be solved. Computational methods that use this approach are called ab initio methods. The theoretical aspects are very well developed and it is in principle known, how to calculate important properties of materials such as the electrical conductivity or the the melting point after solving Schrödinger's equation. However, due to the complexity of this equation for systems containing even a small number of particles, an exact solution for the wavefunction of the system is usually impossible to achieve.

Therefore, certain approximations have to be introduced in order to be able to carry out the simulations. One of the earliest approximations is the Hartree-Fock (HF) method. The HF method aims to approximate the N particle wavefunctions by a single Slater determinant. However, a significant drawback is that it neglects the electron correlation, which leads to considerable deviations from the real energy.

Another method that is extensively used on a wide variety of materials is Density Functional Theory (DFT). Within the DFT approach, the electronic correlation is accounted for in the so called exchange correlation potential. However, an exact analytical form for this potential is not known. It is crucial to find good approximations for the exchange correlation energy in order to yield reasonable results for the energy of the system. The two most prominent approximations of the exchange correlation potential within DFT are the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA).

Even though, LDA and GGA provide good results for a wide range of materials, they do exhibit problems when confronted with strongly correlated systems as well as van der Waals bonded systems. For this reason, it is necessary to come up with computational methods that approximate this strong correlation between electrons, collectively called post-DFT methods. One of these post-DFT methods is the Random Phase Approximation (RPA). In recent years, a lot of research had been conducted on the RPA [1] with one paper highlighting a method to calculate the RPA correlation energy that scales only cubically in system size [2].

Within the RPA, there exists an analytical expression for the correlation energy which depends on the electronic structure factor of the system. This method is already implemented in VASP. The sampling grid of the Brillouin zone used by VASP determines the number of vectors at which the value of the structure factor is calculated. An important property of a computational algorithm is its scaling with a finer sampling of the Brillouin zone. If the computational time increases too much for a finer sampling, then the algorithm can't be used to efficiently predict properties of the system. In the RPA, it is therefore desirable to come up with a way to reduce the computational effort for the structure factor, if a finer sampling grid is chosen. In this thesis, the reduction of the computational effort is achieved by the means of a tricubic spline interpolation. First, exact values of the structure factor are calculated on a coarse grid. Then, the values of the structure factor on the refined grid will be approximated by performing a tricubic spline interpolation. The interpolation is performed for several different materials including both insulators and semiconductors. The convergence of the correlation energy, calculated both with the exact and with the interpolated structure factor, will be investigated for an increasingly refined sampling grid of reciprocal space.

In the first part of this thesis, Kohn Sham DFT will be discussed. This approach maps the problem of finding the wavefunction of a many electron system onto the problem of finding the electron density, depending only on one spatial position. In addition, the interaction energy of the electrons can be described by an effective external potential.

In the next section, the Random Phase Approximation (RPA) will be introduced, within which an analytical expression for the correlation energy will be derived. This can be done by using the Adiabatic Connection Fluctuation Dissipation theorem (ACFDT). This theorem provides a method to calculate the energy of a system by knowing how it reacts to an external perturbation. The linear response function of the system is an important quantity in this approach.

The next section deals with the implementation of the tricubic spline interpolation in VASP. The preliminaries of the interpolation as well as the interpolation algorithm itself will be discussed. Finally, the interpolation algorithm will be tested

for a variety of materials including both isolators and semiconductors. It will be investigated for which materials the interpolation of the structure factor leads to an improved convergence of the RPA correlation energy. These results will be presented in the last chapter.

4 Theory

4.1 Density Functional Theory (DFT)

4.1.1 Introduction

In quantum mechanics, all information about a physical system is encapsulated in the the wavefunction, which can be calculated by solving the Schrödinger equation. In the case of N electrons interacting via the Coulomb force, which are additionally moving in an arbitrary external potential V_{ext}, it takes the following form:

$$H\Psi\left(\vec{r}_1, ..., \vec{r}_N\right) = E\Psi\left(\vec{r}_1, ..., \vec{r}_N\right), \tag{1}$$

with the Hamiltonian H having the form:

$$H = \frac{-\hbar^2}{2m}\sum_{i=1}^{N}\nabla_{\vec{r}_i}^2 + \sum_{i=1}^{N} v_{ext}(\vec{r}_i) + \frac{1}{2}\sum_{i,j=1}^{N}\frac{e^2}{\mid \vec{r}_i - \vec{r}_j \mid} = K + V_{ext} + V_{ee}. \tag{2}$$

The first term in (2), K, corresponds to the kinetic energy of the electrons, V_{ext} describes the influence of an external potential and V_{ee} describes the interaction among the electrons themselves. To avoid confusion, the operator for the external potential will be denoted by capital letters V_{ext} while the specific functional form will be denoted by lowercase letters $v_{ext}(\vec{r})$. While the first and the third term appear for all interacting systems of electrons, it is the second term that determines, what kind of physical system is being considered. For example, in a solid, the external potential is due to the interaction of nuclei with the electrons. V_{ext} would then look like this:

$$V_{ext} = \sum_{i=1}^{N}\sum_{k}\frac{-eQ_k}{\mid \vec{r}_i - \vec{R}_k \mid} = \sum_{i=1}^{N} v_{ext}(\vec{r}_i), \tag{3}$$

where $v_{ext}(\vec{r})$ is given by

$$v_{ext}(\vec{r}) = \sum_{k}\frac{-eQ_k}{\mid \vec{r} - \vec{R}_k \mid}. \tag{4}$$

In equation (3) and (4), the sum over k extends over all nuclei in the solid. Q_k is the charge of the nuclei and $\vec{R}_k$ is their position.
The general approach to a problem like this is to first solve the Schrödinger equation (1), yielding the wave function $\Psi(\vec{r}_1, ..., \vec{r}_N)$. Then, expectation values of all operators can be calculated by evaluating $\langle O\rangle = \langle\Psi|O|\Psi\rangle$.

4.1.2 The Hohenberg Kohn Theorems

By defining $T = K + V_{ee}$, the Hamiltonian (2) can be split up into two parts as follows:

$$H = T + V_{ext}. \tag{5}$$

T has the same form for all N-electron systems and only depends on the number of electrons within the system, N. V_{ext} depends on the choice of $v_{ext}(\vec{r})$. For example, the specific form of $v_{ext}(\vec{r})$ for the interaction between electrons and nuclei is depicted in equation (4). The full Hamiltonian in (5) is therefore uniquely determined by both N and $v_{ext}(\vec{r})$. As a consequence, the ground state $|\Psi_0\rangle$ is also uniquely determined by the same two quantities. From $|\Psi_0\rangle$, the electron density of the ground state can be calculated:

$$n_0(\vec{r}) = \langle\Psi_0|n(\vec{r})|\Psi_0\rangle = N\prod_{i=2}^{N}\int d^3r_i \mid \Psi_0(\vec{r},\vec{r}_2,...,\vec{r}_N) \mid^2, \tag{6}$$

where $n(\vec{r})$ is the electron density operator defined as

$$n(\vec{r}) = \sum_{i=1}^{N}\delta^{(3)}(\vec{r}-\vec{r}_i). \tag{7}$$

This can be seen as follows:

$$\begin{aligned} n_0(\vec{r}) = \langle\Psi_0|n(\vec{r})|\Psi_0\rangle &= \int\prod_{j=1}^{N} d^3r_j\Psi_0^*(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) \\ &\quad \sum_{i=1}^{N}\delta^{(3)}(\vec{r}-\vec{r}_i)\Psi_0(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) = \\ = \sum_{i=1}^{N}\int d^3r_1...d^3r_i...d^3r_N\Psi_0^*(\vec{r}_1,\vec{r}_2,...,\vec{r}_N)&\delta^{(3)}(\vec{r}-\vec{r}_i)\Psi_0(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) = \\ = \sum_{i=1}^{N}\int d^3r_1...d^3r_{i-1}...d^3r_{i+1}...d^3r_N&|\Psi_0(\vec{r}_1,...,\vec{r}_{i-1},\vec{r},\vec{r}_{i+1},...,\vec{r}_N|^2. \end{aligned} \tag{8}$$

For each summand, antisymmetry in both wavefunctions and renaming integration variables can be used which yields the following expression for $n_0(\vec{r})$:

$$n_0(\vec{r}) = N\int\prod_{i=2}^{N} d^3r_i \mid \Psi(\vec{r},\vec{r}_2,...,\vec{r}_N) \mid^2. \tag{9}$$

Therefore, in standard quantum mechanics, both the ground state $|\Psi_0\rangle$ and the ground state density $n_0(\vec{r})$ are functionals of the number of electrons N and of the external potential $v_{ext}(\vec{r})$. Therefore, knowing N and V_{ext}, one can, in principle, calculate expectation values of all observables in question.

Density-functional theory (DFT) provides a different approach for calculating expectation values. This is done by promoting the ground state density to the central object of interest from which all other expectation values of observables can be calculated. DFT reduces the complicated many-body problem, which depends on the

position of all electrons, to a single body problem. The justification for making the ground state density the central object lies in two mathematical statements, the Hohenberg-Kohn theorems. These theorems were published by Hohenberg and Kohn in a paper in 1964 [3] that layed the foundation for DFT.

First Hohenberg Kohn Theorem: *The external potential $v_{ext}(\vec{r})$ is uniquely determined up to a constant by the corresponding ground state density $n_0(\vec{r})$.*

Proof. The statement will be proven by reductio ad absurdum: Suppose that there exist two different external potentials $v_{ext}(\vec{r})$ and $v_{ext}^{'}(\vec{r})$ which both yield the same ground state density $n_0(\vec{r})$. These two potentials result in different Hamiltonians H and $H^{'}$ which yield different ground states $|\Psi_0\rangle$ and $|\Psi_0^{'}\rangle$. The corresponding ground state energies for these two systems are obtained via $E_0 = \langle\Psi_0|H|\Psi_0\rangle$ and $E_0^{'} = \langle\Psi_0^{'}|H^{'}|\Psi_0^{'}\rangle$.
By taking $|\Psi_0^{'}\rangle$ as the trial ground state for the Hamiltonian H, one obtains the following inequality by the variational principle in quantum mechanics:

$$\begin{aligned} E_0 < \langle\Psi_0^{'}|H|\Psi_0^{'}\rangle = \langle\Psi_0^{'}|H^{'}|\Psi_0^{'}\rangle + \langle\Psi_0^{'}|H - H^{'}|\Psi_0^{'}\rangle = E_0^{'} \\ + \int d^3x\, n_0(\vec{r})(v_{ext}(\vec{r}) - v_{ext}^{'}(\vec{r})). \end{aligned} \tag{10}$$

Equivalently, one can take $|\Psi_0\rangle$ as the trial ground state ket for the Hamiltonian $H^{'}$ to obtain another inequality:

$$E_0^{'} < E_0 - \int d^3x\, n_0(\vec{r})(v_{ext}(\vec{r}) - v_{ext}^{'}(\vec{r})). \tag{11}$$

Adding the last two equations yields the following statement, which is the desired contradiction:

$$E_0 + E_0^{'} < E_0 + E_0^{'}. \tag{12}$$

Therefore, there exists a unique (up to a constant) external potential $v_{ext}(\vec{r})$ for a given ground state density $n_0(\vec{r})$. □

The first Hohenberg-Kohn theorem in its formulation above is only valid for non degenerate groundstates. A similar statement holds for degenerate groundstates as well, however the proof is more complicated. The first Hohenberg-Kohn theorem proves that knowledge of the groundstate density $n_0(\vec{r})$ determines the external potential $v_{ext}(\vec{r})$ and the number of electrons N by integrating over the density. Vice versa, knowledge of $v_{ext}(\vec{r})$ and N also determines $n_0(\vec{r})$. As N is a functional of $n_0(\vec{r})$, also the operators K and V_{ee} are functionals of the density. One can therfore formally define the following functional $T[n]$ that gives the correct sum of the kinetic and interaction energy for a given groundstate density.

$$T[n(\vec{r})] = \langle \Psi | \, K + V_{ee} \, | \Psi \rangle \, . \tag{13}$$

However, only the existence of this functional can be guaranteed, its explicit form is unknown.

A density $n(\vec{r})$ that is the ground state density for some external potential $v(\vec{r})$ is called v-representable [4]. For such densities one can define an energy functional $E_V[n]$ by:

$$E_V[n] = T[n] + \int d^3r v(\vec{r}) n(\vec{r}), \tag{14}$$

where $T[n] = \langle \Psi[n] | \, \hat{T} \, | \Psi[n] \rangle$ as in (13). Since $n(\vec{r})$ is v-representable, it determines both the number of electrons N and the external potential $V(\vec{r})$ which are used to calculate the ground state $|\Psi[n]\rangle$. The second Hohenberg-Kohn theorem makes a claim about the minimisation of the energy functional of equation (14).

Second Hohenberg Kohn theorem: *Let $v(\vec{r})$ be an external potential in which N electrons move and E_0 the corresponding ground state energy for this system. Then $\forall$ v-representable ground state densities $n(\vec{r})$ ($\exists$ an external potential $v_{ext}(\vec{r})$ such that solving the Schrödinger equation yields $n(\vec{r})$ as a solution for the density), it holds that $E_V[n] \geq E_0$, with equality holding only for the true ground state density.*

Proof. Any given ground state density $n(\vec{r})$ determines by the first Hohenberg-Kohn theorem in principal its corresponding external potential $v_{ext}(\vec{r})$. Solving the Schrödinger equation with this external potential yields a ground state $|\Psi\rangle$, which can be used as a trial state for the ground state of the system governed by the fixed potential $V(\vec{r})$:

$$\begin{aligned} E_V[n] = T[n] + \int d^3r v(\vec{r}) n(\vec{r}) = \langle \Psi[n] | \, \hat{T} \, | \Psi[n] \rangle + \langle \Psi[n] | \, \hat{V} \, | \Psi[n] \rangle = \\ = \langle \Psi[n] | \, \hat{H} \, | \Psi[n] \rangle \geq E_0. \end{aligned} \tag{15}$$

The inequality follows from the variational principle in quantum mechanics. It states that the functional $\epsilon[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$ attains its minimum value only for the exact ground state of the system. The functional will yield greater energies for all other trial ground states.

If the trial density is the actual ground state density $n_0(\vec{r})$ of the system, it will yield the potential $v(\vec{r})$. Solving Schrödinger's equation will then lead to the true ground state $|\Psi_0\rangle$. Plugging the actual density into the energy functional as in equation

(15) yields the equality:

$$E_V[n_0] = \langle \Psi[n_0] | \hat{H} | \Psi[n_0] \rangle = E_0. \tag{16}$$

□

To sum it up, the previous theorem states that there exists an energy functional $E_V[n]$ which assumes its minimum value for the correct groundstate density n for the given external potential v. Minimising this functional under the constraint of fixed particle number N yields the ground state energy of the system.

4.1.3 Kohn Sham DFT

The second Hohenberg-Kohn theorem states that the ground state energy of a system can be found by minimizing its energy functional given by equation (14). The problem with this approach though is that the functional $T[n]$ is not known analytically as it contains the interaction between the electrons. Thus, one has to somehow approximate the functional $T[n]$ in order to achieve reliable results for the groundstate energy of the system.
This section deals with one way to approach this problem by mapping the system of interacting particles onto a system of non interacting particles with the same density. This is done by constructing an effective external potential $v_{eff}^{KS}(\vec{r})$, which accounts for the interaction between the electrons. In what follows, I will largely follow the paper of Kohn and Sham who came up with this approach first in 1965 [5]:
By rewriting the energy functional of equation (14), the ground state energy of a system of interacting electrons moving in an external potential $v_{ext}(\vec{r})$ can be written as

$$E[n] = \int d^3r v_{ext}(\vec{r}) n(\vec{r}) + \frac{1}{2} \int d^3\vec{r} d^3\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} + G[n], \tag{17}$$

where $G[n]$ is a functional of the density which will contain the major parts due to the interaction. It can be written as

$$G[n] = T[n] - \frac{1}{2} \int d^3\vec{r} d^3\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid}, \tag{18}$$

after comparing with the original energy functional in (14). The first summand of equation (17) is the energy of the system due to the external potantial, the second term describes the classical electrostatic energy of the system and is called the Hartree term $E_H[n]$.
Kohn and Sham proposed to split up the functional $G[n]$ as follows:

$$G[n] = T_s[n] + E_{xc}[n]. \tag{19}$$

$T_s[n]$ is the kinetic energy of a system of non interacting electrons with the density $n(\vec{r})$. It follows from the first Hohenberg-Kohn theorem that the kinetic energy is a functional of the density since the wavefunction itself is a functional of the density. $E_{xc}[n]$ is the exchange correlation functional. It comprises all energy contributions which cannnot be accounted for by the classical Coulomb interaction. The problem lies in the fact that in general there is no exact analytical expression for $E_{xc}[n]$ for an arbitrary density n. The challenge is therefore to find good approximations for the exchange-corrleation functional. One of these approximations is the so called local density approximation (LDA). The LDA assumes that the density is only varying slowly. It makes it possible to write down an approximate expression for $E_{xc}[n]$.
The LDA and another method to approximate the exchange-correlation energy will be discussed at the end of this chapter. For now, it is assumed that an exact expression for $E_{xc}[n]$ is known, and the theory will be developed from there.
The mapping of the interacting system of electrons onto the non interacting system governed by an external potential $v_{eff}^{KS}(\vec{r})$ can be achieved by writing down the variational problem for the energy functional $E_V[n]$. It reaches its stationary value for the true groundstate density, which can be found by setting its functional derivative equal to zero:

$$\frac{\delta}{\delta n(\vec{r})}\left(T[n] + \int d^3r v_{ext}(\vec{r})n(\vec{r}) - \alpha\left(\int d^3r n(\vec{r}) - N\right)\right) = 0. \tag{20}$$

α is a Lagrange multiplier specifying that the minimisation of $E_V[n]$ runs over all densities that yield the correct number of particles when intergrated over the whole space.
By taking the functional derivative with respect to $n(\vec{r})$ of equation (20), one obtains:

$$\frac{\delta T_s[n]}{\delta n(\vec{r})} + \int d^3\vec{r}' \frac{n(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} + v_{ext}(\vec{r}) = \alpha. \tag{21}$$

The external effective Kohn-Sham potential is now defined as

$$v_{eff}^{KS}(\vec{r}) = \int d^3r' \frac{n(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} + v_{ext}(\vec{r}), \tag{22}$$

such that the variational problem of equation (20) finally reads:

$$\frac{\delta T_s[n]}{\delta n(\vec{r})} + v_{eff}^{KS}(\vec{r}) = \alpha. \tag{23}$$

The first part of equation (23) is the functional derivative of the kinetic energy of a non interacting system of electrons. The second part is the desired external

potential which mimics the interaction between the electrons. Equation (23) is the same equation that describes a system of non-interacting electrons moving in an external potantial V_{eff}^{KS}. This can be seen by first writing down the Hamiltonian for such a system:

$$H = T_s + V_{eff}^{KS}. \tag{24}$$

In order to find the corresponding variational equation out of this Hamiltonian, one has to write down the energy functional for this system:

$$E_{V_{eff}^{KS}}[n] = T_s[n] + \int d^3\vec{r} v_{eff}^{KS}(\vec{r}) n(\vec{r}). \tag{25}$$

This time, however, the functional $T_s[n]$ is in fact known analytically since it does not contain any interaction terms. Thus, finding the true groundstate density by minimising the energy functional under the constraint of fixed particle number N can be carried out easily:

$$\frac{\delta}{\delta n(\vec{r})}\left(T_s[n] + \int d^3\vec{r} v_{eff}^{KS}(\vec{r}) n(\vec{r}) - \alpha\left(\int d^3 r n(\vec{r}) - N\right)\right) = 0. \tag{26}$$

Rearranging terms then leads to the same equation as in (23). Thus, it was shown that the Kohn-Sham approach reduces the interacting N-particle problem onto a non interacting 1-particle problem. The independent particle Schrödinger equation for this system looks as follows:

$$\left(-\frac{1}{2}\nabla^2 + v_{eff}^{KS}(\vec{r})\right)\Psi_i^{KS}(\vec{r}) = \epsilon_i \Psi_i^{KS}(\vec{r}), \tag{27}$$

with ϵ_i being the 1-particle eigenenergies and Ψ_i^{KS} being the corresponding eigenfunctions. The ground state of a fermionic system of N particles is now obtained by filling each of the N lowest eigenstates with one particle, since Pauli's exclusion principle states that two fermions cannot be simultaneously in a state with the same quantum numbers. The groundstate wavefunction $\Psi_0(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$ is therefore the Slater determinant of the first N eigenfunctions $\Psi_i^{KS}(\vec{r}_i)$ for $i = 0, ..., N-1$.

However, the problem lies in the fact that the effective potential V_{eff}^{KS} is itself dependent on the electron density of the system. This makes it necessary to solve the Kohn-Sham equations self consistently. At first, an initial density needs to be chosen in order to calculate the effective potential. Then the Kohn-Sham equations will be solved using this potential, yielding a set of eigenfunctions Ψ_i^{KS}. By using equation (6), a new groundstate density can be constructed, which is then used to calculate a new potential. This procedure will be iterated until the density does not change anymore from one iteration step to the next.

As mentioned before, the previous calculations relied on the fact that an exact expression for the exchange correlation energy $E_{xc}[n]$ is known. It is therefore crucial to find good approximations for the exchange correlation functional, the simplest of which is the LDA. In the LDA, the exchange correlation functional is approximated by the following integral:

$$E_{xc}^{LDA}[n] = \int d^3r n(\vec{r}) \epsilon_{xc}^{LDA}(n(\vec{r})). \tag{28}$$

First of all, it is important to notice that $E_{xc}^{LDA}[n]$ depends only on the value of the density itself. At every point, locally, a homogeneous density is assumed. Secondly, in the effective potential V_{eff}^{KS} of equation (22), only the functional derivative of the exchange correlation $\frac{\delta E_{xc}[n]}{\delta n(\vec{r})}$ occurs, which is, in the case of LDA [4]:

$$v_{xc}^{LDA}(\vec{r}) = \frac{\delta E_{xc}^{LDA}[n]}{\delta n(\vec{r})} = \epsilon_{xc}^{LDA}(n(\vec{r})) + n(\vec{r}) \frac{\partial \epsilon_{xc}^{LDA}(n)}{\partial n}|_{n=n(\vec{r})}. \tag{29}$$

$\epsilon_{xc}^{LDA}(n(\vec{r}))$ is the exchange correlation energy per particle in the uniform electron gas (UEG) and will be denoted $\epsilon_{xc}^{UEG}(n(\vec{r}))$ from now on. The UEG is a model of N electrons confined in a volume V together with a positive background charge that is uniformly distributed within the volume. The positive background charge is supposed to mimic the nuclei in a solid. The electron density of such a system is therefore simply $n(\vec{r}) = \frac{N}{V} = const.$ Although there are different physical models, on which the LDA can be based, the UEG is the most common one. $\epsilon_{xc}^{UEG}[n]$ can be seperated into an exchange part $\epsilon_{x}^{UEG}[n]$ and a correlation part $\epsilon_{c}^{UEG}[n]$. In the UEG model, there exists an exact form for the exchange part [6]:

$$\epsilon_{x}^{UEG}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} n(\vec{r})^{\frac{1}{3}}. \tag{30}$$

Analytical expressions for the correlation energy per particle in the UEG are only known in high-density and low-density limiting cases. For intermediate density values, quantum Monte Carlo simulations have been performed to calculate the correlation energy [7]. Usually, the modus operandi is to interpolate between the energy values obtained via Monte Carlo simulations with the requirement of reproducing the analytically known correlation functionals in the limiting cases. An example of an analytical correlation functional obtained in the way explained above, is the following [8]:

$$\epsilon_{c}^{UEG} = a \cdot ln\left(1 + \frac{b}{r_s} + \frac{b}{r_s^2}\right). \tag{31}$$

r_s is the Wigner Seitz parameter. It is defined by $\frac{1}{\rho} = \frac{4\pi {r_s}^3}{3}$. The Wigner Seitz parameter therefore determines the mean volume of a particle in the UEG.

Another way to approximate the exchange correlation functional $E_{xc}[n]$ is to use the so called generalized gradient approximation (GGA). In the LDA, a homogenous electron density is assumed. Although LDA yields quite accurate results for some systems, the assumption of constant density is not true for real systems and will yield errors. To correct these mistakes, one also wants to include information about the change of the density. This is done by additionally including a dependency on the gradient of the density in the exchange correlation functional. The GGA functional is then given by integrating over a function f depending on both n and ∇n:

$$E_{xc}^{GGA}[n] = \int d^3\vec{r} f\left(n, \nabla n\right). \tag{32}$$

There exist different implementations of GGA functionals, with most relying on known sum rules and exact constraints. A prominent example is the PBE functional derived by Perdew et al. [9].

4.2 The Random Phase Approximation (RPA)

4.2.1 Introduction

In the last section, Kohn Sham density functional theory was introduced in order to map the problem of interacting electrons in an external potential onto a system in which the interaction is replaced by an effective potential. The challenge of this approach lies in the difficulty to find good approximations for the exchange correlation energy E_{xc}. LDA and GGA are two such methods that yield analytical expressions for the exchange correlation energy.
In this chapter, the more advanced Random Phase Approximation (RPA) will be discussed. It will be shown that E_{xc} can be split up into two parts, the exchange part E_x and the correlation part E_c with the latter taking the following form [1] [10]:

$$E_c = \int_0^\infty \frac{d\omega}{2\pi} Tr(ln(1 - \chi^{KS} v) + \chi^{KS} v), \tag{33}$$

where v is the Coulomb potential and χ^{KS} is the linear response function of the Kohn Sham system, which describes changes in the groundstate density of the system due to fluctuations of the external potential. The Adiabatic Connection Fluctuation Dissipation Theorem (ACFDT) will be used to arrive at this result. The idea of the ACFDT approach is to introduce a switching parameter λ which connects the fully interacting Hamiltonian (2) continuously with the Kohn Sham Hamiltonian (24).
In the following, the expression for the response function of the Kohn Sham system χ^{KS} will be derived. Additionally a chapter about time dependent perturbation theory is included. At the end, the ACFDT approach will be discussed leading to the expression for E_c in the RPA.
We will follow [10] for the most part here. A similar derivation can be found in [11].

4.2.2 Linear Response Theory

The first Hohenberg Kohn theorem states that there exists a one to one correspondence between the external potential V_{ext} acting on a system and its ground state density. Often, the external potential is time dependent. The question then is how the ground state density changes when it is affected by this time dependent perturbation. If the change of the external potential is weak, the induced change in the ground state density is linearly dependent on the perturbation. This linear dependency of the groundstate density on the external perturbation can be described by the linear response function χ:

$$\delta n(\vec{r}, t) = \int dt' d^3\vec{r}' \chi(\vec{r}, \vec{r}', t - t') \delta v_{ext}(\vec{r}', t'). \tag{34}$$

$\delta n(\vec{r},t)$ is the change in the groundstate density, while $\delta V_{ext}(\vec{r},t)$ is the change in the external potential. Taking the functional derivative of the change of density with respect to the change in the external potential yields the response function:

$$\chi(\vec{r},\vec{r}',t-t') = \frac{\delta n(\vec{r},t)}{\delta v_{ext}(\vec{r}',t')} \tag{35}$$

The same formalism can be applied to the Kohn Sham system, in which the particles do not interact with each other. All of the interaction is compressed in the effective external Kohn Sham potential V_{eff}^{KS}. The Kohn Sham response function describes the induced change in the density due to a varying external effective Kohn Sham potential:

$$\delta n(\vec{r},t) = \int dt' d^3\vec{r}' \chi^{KS}(\vec{r},\vec{r}',t-t')\delta v_{eff}^{KS}(\vec{r}',t'). \tag{36}$$

The Kohn Sham response function can be obtained through a functional derivative as well.

The aim is to find an equation that links the response function of the fully interacting system χ to the response function of the Kohn Sham system χ^{KS}.

Regardless of which approach is chosen, the change in the density needs to be the same for both systems. Therefore, using equation (22) to substitute $v_{eff}^{KS}(\vec{r}',t')$, one can equate equations (34) and (36) which yields:

$$\int dt' d^3\vec{r}' \chi(\vec{r},\vec{r}',t-t')\delta v_{ext}(\vec{r}',t') = \int dt' d^3\vec{r}' \chi^{KS}(\vec{r},\vec{r}',t-t')(\delta v_{ext}+\delta v_H+\delta v_{xc})(\vec{r}',t'). \tag{37}$$

In order to be able to compare coefficients in the equation above, one needs to apply the chain rule to δV_H and δV_{xc} to find their dependencies on δV_{ext}. This is done as follows:

$$\delta v_H(\vec{r}',t') = \int dt_1 dt_2 d^3\vec{r}_1 d^3\vec{r}_2 \frac{\delta v_H(\vec{r}',t')}{\delta n(\vec{r}_1,t_1)} \frac{\delta n(\vec{r}_1,t_1)}{\delta v_{ext}(\vec{r}_2,t_2)} \delta v_{ext}(\vec{r}_2,t_2) \tag{38}$$

where

$$\frac{\delta v_H(\vec{r}',t')}{\delta n(\vec{r}_1,t_1)} = \frac{\delta}{\delta n(\vec{r}_1,t_1)} \int d^3\vec{r}'' dt'' \frac{n(\vec{r}'',t'')}{\mid \vec{r}'(t') - \vec{r}''(t'') \mid} = \frac{1}{\mid \vec{r}'(t') - \vec{r}_1(t_1) \mid} \tag{39}$$

and $\frac{\delta n(\vec{r}_1,t_1)}{\delta V_{ext}(\vec{r}_2,t_2)}$ is the response function as in equation (35). The same needs to be done for δV_{xc}:

$$\delta v_{xc}(\vec{r}',t') = \int dt_1 dt_2 d^3\vec{r}_1 d^3\vec{r}_2 \frac{\delta v_{xc}(\vec{r}',t')}{\delta n(\vec{r}_1,t_1)} \frac{\delta n(\vec{r}_1,t_1)}{\delta v_{ext}(\vec{r}_2,t_2)} \delta V_{ext}(\vec{r}_2,t_2) \tag{40}$$

In order to evaluate this expression, one needs to introduce the exchange correlation kernel f_{xc}. It is defined as the functional derivative of the exchange correlation potential with respect to the density:

$$f_{xc}(\vec{r}, \vec{r}', t - t') = \frac{\delta v_{xc}(\vec{r}, t)}{\delta n(\vec{r}', t')}. \tag{41}$$

The results of equations (38) and (40) can now be plugged back into (37). After switching from time dependent response functions to frequency dependent response functions through a Fourier transform and renaming integration variables, one obtains the following equation:

$$\begin{aligned}\chi(\vec{r}, \vec{r}', \omega) = \chi^{KS}(\vec{r}, \vec{r}', \omega) + \\ \int d^3\vec{r}_1 d^3\vec{r}_2 \chi^{KS}(\vec{r}, \vec{r}_1, \omega) \left(\frac{1}{\mid \vec{r}_1 - \vec{r}_2 \mid} + f_{xc}(\vec{r}_1, \vec{r}_2, \omega) \right) \chi(\vec{r}_2, \vec{r}', \omega).\end{aligned} \tag{42}$$

This equation is called Dyson's equation. In order to calculate the response function of the fully interacting system, one needs to calculate the response function of the non interacting KS system first and then use an approximation for the exchange correlation kernel f_{xc} in Dyson's equation.
The response function of the Kohn Sham system $\chi^{KS}(\vec{r}, \vec{r}', \omega)$ is a key quantity for developing the formalism of the RPA. The next section deals with time dependent perturbation theory, which will be helpful for the derivation of χ^{KS}.

4.2.3 Time Dependent Perturbation Theory

Consider a time dependent Hamiltonian which is given by the following equation:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t). \tag{43}$$

$\hat{H}_0$ is the initial time independent Hamiltonian, and $\hat{V}(t)$ is a time dependent perturbation which makes the full Hamiltonian $\hat{H}(t)$ of the system also time dependent. In the Schrödinger picture, one would solve Schrödinger's equation of motion $i\partial_t \left|\Psi(t)\right\rangle_S = \hat{H}(t) \left|\Psi(t)\right\rangle_S$.
However, in the case where there is only a time dependent perturbation it is more convenient to switch to the so called interaction picture, where the time dependency is defined as follows:

$$\left|\Psi(t)\right\rangle_I = e^{i\hat{H}_0 t} \left|\Psi(t)\right\rangle_S. \tag{44}$$

In a picturesque way, one can think of this as removing the time dependency that stems from $\hat{H}_0$ and only considering the time evolution due to the potential $\hat{V}(t)$. The state in the interaction picture therefore only considers the time dependency of

the perturbation $\hat{V}(t)$. It obeys a slightly different equation of motion that can be derived easily from Schrödinger's equation.:

$$\begin{aligned} i\partial_t \left|\Psi(t)\right\rangle_I &= -\hat{H}_0 e^{i\hat{H}_0 t}\left|\Psi(t)\right\rangle_S + e^{i\hat{H}_0 t} i\partial_t \left|\Psi(t)\right\rangle_S = \\ &= e^{i\hat{H}_0 t}\left(-\hat{H}_0 + \hat{H}(t)\right)\left|\Psi(t)\right\rangle_S = \hat{V}_I(t)\left|\Psi(t)\right\rangle_I . \end{aligned} \tag{45}$$

The structure of the equation of motion is the same as in the Schrödinger equation, only with $\hat{H}(t)$ replaced by $\hat{V}_I(t) = e^{i\hat{H}_0 t}\hat{V}(t)e^{-i\hat{H}_0 t}$.
As in the Schrödinger picture, there also exists a time evolution operator $\hat{U}_I(t, t_0)$ in the interaction picture, which relates the time dependent state $\left|\Psi(t)\right\rangle_I$ to some initial state $\left|\Psi(t_0)\right\rangle_I$. It obeys the following equation of motion with the usual boundary condition that $\hat{U}_I(t_0, t_0) = \mathbb{1}$.

$$i\partial_t \hat{U}_I(t, t_0) = \hat{V}_I(t)\hat{U}_I(t, t_0). \tag{46}$$

One can easily check that the time evolution operator is then given by:

$$\hat{U}_I(t, t_0) = \mathbb{1} - i\int_{t_0}^{t} dt' \hat{V}_I(t')\hat{U}_I(t', t_0). \tag{47}$$

This is a self consistent equation for $\hat{U}_I(t, t_0)$ which can be solved by plugging in this very expression for $\hat{U}_I(t', t_0)$ under the integral sign.

$$\hat{U}_I(t, t_0) = \mathbb{1} - i\int_{t_0}^{t} dt' \hat{V}_I(t')\left(\mathbb{1} - i\int_{t_0}^{t'} dt'' \hat{V}_I(t'')\hat{U}_I(t'', t_0)\right). \tag{48}$$

Iterating this procedure an infinite number of times, the formal solution for the time evolution operator in the interaction picture can be written as:

$$\hat{U}_I(t, t_0) = \mathbb{1} + \sum_{n=1}^{\infty}(-i)^n \int_{t_0}^{t} dt_1 ... \int_{t_0}^{t_{n-1}} dt_n \hat{V}_I(t_1)...\hat{V}_I(t_n). \tag{49}$$

Note that the operators in the integrand are ordered in time. That means that the operators are arranged in such a way that an operator with a greater time argument is always left to an operator with a smaller time argument. Therefore, the operator with the greatest time argument is located before all other operators. This time ordered sequence is given by $t_0 < t_n < t_{n-1} < ... < t_1 < t$. With this insight, the time evolution operator can be written in a more compact way using the time ordering symbol $\mathcal{T}$.

$$\hat{U}_I(t, t_0) = \mathcal{T}\left[e^{-i\int_{t_0}^{t} dt' \hat{V}_I(t')}\right] \tag{50}$$

The exponential function of operators is defined through its Taylor series. The time ordering symbol acts on each term of the Taylor series separately. One can

check that this is the actual solution for equation (46) by plugging it in:

$$\begin{aligned} i\partial_t \hat{U}_I(t,t_0) &= i\partial_t \left(\mathbb{1} + \sum_{n=1}^{\infty} (-i)^n \int_{t_0}^{t} dt_1 ... \int_{t_0}^{t_{n-1}} dt_n \hat{V}_I(t_1)...\hat{V}_I(t_n) \right) \\ &= \hat{V}_I(t) \sum_{n=1}^{\infty} (-i)^{n-1} \int_{t_0}^{t} dt_2 ... \int_{t_0}^{t_{n-1}} dt_n \hat{V}_I(t_2)...\hat{V}_I(t_n) = \hat{V}_I(t)\hat{U}_I(t,t_0). \end{aligned} \tag{51}$$

First, one uses that the only dependency on t is in the upper integral limit of the integral farthest to the left. Then indices are being renamed to see that the infinite sum yields again the time evolution operator.

Suppose that the stationary Schrödinger equation for the time independent part of the Hamiltonian $\hat{H}_0$ is already solved, yielding a complete set of orthonormal eigenkets $\{|n\rangle\}$ and a set of eigenenergies $\{E_n\}$ satisfying the equation $\hat{H}_0 |n\rangle = E_n |n\rangle$, then an arbitrary state $|\Psi\rangle$ can be expanded in this basis: $|\Psi\rangle = \sum_n c_n |n\rangle$. The time evolution of a state in this system is given by $|\Psi(t)\rangle = \sum_n c_n(t) |n\rangle = \sum_n c_n e^{-iE_n t} |n\rangle$.

Consider now a perturbed system in which the Hamiltonian looks like equation (43). An arbitrary time dependent state $|\Psi(t)\rangle$ in this system can also be expanded as a linear combination of the eigenbasis $\{|n\rangle\}$:

$$|\Psi(t)\rangle = \sum_n c_n(t) e^{-iE_n t} |n\rangle \tag{52}$$

The phase factor included in the above sum takes care of the time evolution due to the original time independent Hamiltonian $\hat{H}_0$, whereas $c_n(t)$ will depend on the perturbing potential $\hat{V}(t)$. The aim is now to determine the expansion coefficients $c_n(t)$. This can be done by considering the system being initially prepared in state $|i\rangle$ at time $t_0 = 0$. The time evolution of this state can be calculated using the time evolution operator as given in equation (50).

$$|i(t)\rangle = \hat{U}_I(t,t_0) |i\rangle = \sum_n |n\rangle \langle n| \hat{U}_I(t,t_0) |i\rangle = \sum_n c_n(t) |n\rangle \tag{53}$$

The expansion coefficients $c_n(t)$ for the potential are therefore given by:

$$\begin{aligned} c_n(t) = \langle n| \hat{U}_I(t,t_0) |i\rangle = \langle n| \mathcal{T} \left[e^{-i\int_{t_0}^{t} dt' \hat{V}_I(t')} \right] |i\rangle = \delta_{ni} - i \int_{t_0}^{t} dt' \langle n| \hat{V}_I(t') |i\rangle \\ - \sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \langle n| \hat{V}_I(t') |m\rangle \langle m| \hat{V}_I(t'') |i\rangle + \mathcal{O}(\hat{V}_I{}^3) = \\ = c_n^{(0)}(t) + c_n^{(1)}(t) + c_n^{(2)}(t) + \mathcal{O}(\hat{V}_I{}^3) \end{aligned} \tag{54}$$

The physical interpretation of $\langle n|\,\hat{U}_I(t,t_0)\,|i\rangle$ is the probabilty amplitude, to find the state $|i\rangle$ in state $|n\rangle$ after a time difference of $t-t_0$ due to a perturbation $\hat{V}(t)$. In the equation above, only the first two summands of the Taylor series of the time evolution operator in the interaction picture were explicitely considered. The expansion coefficients $c_n(t)$ are now being written as a perturbation series $c_n(t) = \sum_{i=0}^{\infty} c_n^{(i)}(t)$, where each summand corresponds to an element in the Taylor series expansion of the time evolution operator $\hat{U}_I(t,t_0)$.
The coefficients $c_n^{(i)}(t)$ of the perturbation series are given by comparing coefficients with the Taylor series expansion of the transition amplitude $\langle n|\,\hat{U}_I(t,t_0)\,|i\rangle$ which is given by equation (54):

$$\begin{aligned} c_n^{(0)} &= \delta_{ni} \\ c_n^{(1)} &= -i\int_{t_0}^{t} dt' e^{i\omega_{ni}t'} V_{ni}(t') \\ c_n^{(2)} &= -\sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' e^{i\omega_{nm}t'} e^{i\omega_{mi}t''} V_{nm}(t')V_{mi}(t'') \end{aligned} \tag{55}$$

Here we have used that $\hat{V}_I(t) = e^{i\hat{H}_0 t}\hat{V}(t)e^{-i\hat{H}_0 t}$ and defined $\omega_{nm} = E_n - E_m$ as the energy difference between two states. Additionally, the abbreviation $V_{nm}(t) = \langle n|\,\hat{V}(t)\,|m\rangle$ is used.

4.2.4 Response function for the Kohn-Sham system

In this section, an explicit expression for the Kohn Sham response function χ^{KS} will be derived [10]. The effects of fluctuations of the external potential will be considered for a general system of interacting particles first. Then the focus will be put on the Kohn Sham system of non interacting particles.
An expression for the response function can be derived by considering a time dependent change to the external potential $\delta v_{ext}(\vec{r},t)$. This change in the potential affects all particles within the system. Therefore, the change in the Hamiltonian can be written as

$$\delta\hat{H}(t) = \sum_{i=1}^{N} \delta v_{ext}(\vec{r}_i,t), \tag{56}$$

where the summation over i runs over all N particles in the system.
Additionally, an adiabatic switching parameter $e^{\eta t}$ will be introduced that allows to switch between the perturbed and unperturbed system. For $t\to-\infty$, the perturbation vanishes and the Hamiltonian is unperturbed. For $t\to 0$, the full effect of the perturbation is felt by the system. The change in the Hamiltonian then reads:

$$\delta\hat{H}(t) = e^{\eta t}\sum_{i=1}^{N}\delta v_{ext}(\vec{r}_i, t), \tag{57}$$

where η is a positive real number between 0 and 1.
This is a practical example of a perturbation as it appeared generally in the previous chapter. The full Hamiltonian of the system does now look like $\hat{H}(t) = \hat{H}^0 + \delta\hat{H}(t)$. Furthermore, suppose that the stationary Schrödinger equation for the unperturbed Hamiltonian $\hat{H}^0$ is already solved and its eigenvalue equation reads $\hat{H}^0\left|\Psi_n^0\right\rangle = E_n^0\left|\Psi_n^0\right\rangle$. Here, the uppercase 0 denotes the unperturbed system, while the lowercase n denotes the n-th eigenstate and eigenenergy.
The goal is now to find the solutions to the time dependent Schrödinger equation for the perturbed system:

$$i\partial_t\left|\Psi(t)\right\rangle = \left(\hat{H}_0 + \delta\hat{H}(t)\right)\left|\Psi(t)\right\rangle. \tag{58}$$

In the previous chapter, it was argued (see equation (52)) that such a time dependent eigenstate can be expanded in the complete set of eigenstates of the unperturbed Hamiltonian. The expansion coefficients depending on the applied perturbation will be replaced by the perturbation series truncated after the second term:

$$\left|\Psi(t)\right\rangle = \sum_n c_n(t)e^{-iE_n^0 t}\left|\Psi_n^0\right\rangle = \sum_n\left(c_n^{(0)}(t) + c_n^{(1)}(t)\right)e^{-iE_n^0 t}\left|\Psi_n^0\right\rangle. \tag{59}$$

If the initial state of the system was the ground state before the perturbation was applied, the expansion coefficients that determine the time dependent state can be calculated as follows:

$$\begin{aligned}\left|\Psi(t)\right\rangle = \sum_n\left(\delta_{n0} - i\int_{t_0}^{t}dt'e^{i\omega_{n0}t'}\delta\hat{H}_{n0}(t')\right)e^{-iE_n^0 t}\left|\Psi_n^0\right\rangle = \\ = e^{-iE_n^0 t}\left|\Psi_0^0\right\rangle + \sum_n c_n^{(1)}(t)e^{-iE_n^0 t}\left|\Psi_n^0\right\rangle.\end{aligned} \tag{60}$$

The next step is to evaluate the integral determining the coefficient $c_n^{(1)}(t)$. To do this, it will be useful to express the perturbation $\delta\hat{H}(t) = e^{\eta t}\sum_{i=1}^{N}\delta v_{ext}(\vec{r}_i, t)$ by its Fourier representation. This can be done by using the density operator $\hat{n}(\vec{r}) = \sum_{i=1}^{N}\delta^{(3)}(\vec{r}-\vec{r}_i)$. I will state the Fourier representation of the perturbation and show that it is equivalent to the original perturbation:

$$\delta\hat{H}(t) = \int d^3\vec{r} \int \frac{d\omega}{2\pi} e^{-i\tilde{\omega}t} \delta v_{ext}(\vec{r},\omega)\hat{n}(\vec{r}) = \int d^3\vec{r} \int \frac{d\omega}{2\pi} e^{-i\tilde{\omega}t} \delta v_{ext}(\vec{r},\omega) \sum_{i=1}^{N} \delta^{(3)}(\vec{r}-\vec{r}_i)$$
$$= e^{\eta t} \sum_{i=1}^{N} \int d^3\vec{r} \int \frac{d\omega}{2\pi} e^{-i\omega t} \delta v_{ext}(\vec{r},\omega)\delta^{(3)}(\vec{r}-\vec{r}_i) = e^{\eta t} \sum_{i=1}^{N} \delta V_{ext}(\vec{r}_i,t). \tag{61}$$

Throughout the calculation, we used that $\tilde{\omega} = \omega + i\eta$. Using equation (61) and (55), $c_n^{(1)}(t)$ can now be calculated:

$$\begin{aligned} c_n^{(1)}(t) &= -i \int_{-\infty}^{t} dt' e^{i\omega_{n0}t'} \langle \Psi_n^0 | \, \delta\hat{H}(t') \, | \Psi_0^0 \rangle = \\ &= -i \int d^3\vec{r}' \int \frac{d\omega}{2\pi} \int_{-\infty}^{t} dt' e^{i(\omega_{n0}-\tilde{\omega})t'} \delta v_{ext}(\vec{r}',\omega) \langle \Psi_n^0 | \, \hat{n}(\vec{r}') \, | \Psi_0^0 \rangle \\ &= -\int d^3\vec{r}' \int \frac{d\omega}{2\pi} \delta v_{ext}(\vec{r}',\omega) \langle \Psi_n^0 | \, \hat{n}(\vec{r}') \, | \Psi_0^0 \rangle \, \frac{e^{i(\omega_{n0}-\tilde{\omega})t}}{\omega_{n0}-\tilde{\omega}}. \end{aligned} \tag{62}$$

In the last step, the integration over the parameter t' was performed.
The response function determines the effect that a change in the external potential, such as $\delta\hat{H}(t)$, has on the electron density. The time dependent electron densities can now be computed for both the unperturbed system and the perturbed system, assuming that at time t_0, the system assumed the ground state of the unperturbed Hamiltonian $|\Psi_0^0\rangle$. The difference between the two densities will yield the time dependent density change $\delta n(\vec{r},t)$ due to the external perturbation.
The time evolution in the unperturbed system is given by applying the unitary time evolution operator to the ground state: $|\Psi_0^0(t)\rangle = e^{-iE_0^0 t} |\Psi_0^0\rangle$. The density is then given by calculating the expectation value of the density operator $n(\vec{r},t) = \langle \Psi_0^0(t) | \, \hat{n}(\vec{r}) \, | \Psi_0^0(t) \rangle$. The density in the perturbed system is given by replacing the time dependent ket $|\Psi_0^0(t)\rangle$ with $|\Psi(t)\rangle$ given by equation (60) in the expectation value for the density operator.
The change in density due to the external perturbation is then given as follows:

$$\delta n(\vec{r},t) = \langle \Psi(t) | \, \hat{n}(\vec{r}) \, | \Psi(t) \rangle - \langle \Psi_0^0(t) | \, \hat{n}(\vec{r}) \, | \Psi_0^0(t) \rangle \, . \tag{63}$$

Plugging in the expression for the time dependent state in the perturbed system given by equation (60), the density change can be written as

$$\delta n(\vec{r},t) = \sum_{n\neq 0} \left(c_n^{(1)}(t) e^{-i\omega_{n0}t} \langle \Psi_0^0 | \, \hat{n}(\vec{r}) \, | \Psi_n^0 \rangle + c_n^{(1)}(t)^* e^{-i\omega_{0n}t} \langle \Psi_n^0 | \, \hat{n}(\vec{r}) \, | \Psi_0^0 \rangle \right). \tag{64}$$

Terms of order $\mathcal{O}(c_n^{(1)})^2$ and higher order terms have been neglected in this calculation as they will become irrelevant once the functional derivative of δn is being calculated. The next step is to plug in the explicit expressions for the coefficients $c_n^{(1)}(t)$ and its complex conjugate that were derived in equation (62). The density change can then be rewritten as

$$\begin{aligned}\delta n(\vec{r},t) = &-\sum_{n\neq 0}\int d^3\vec{r}' \int \frac{d\omega}{2\pi} e^{-i\tilde{\omega}t}\delta v_{ext}(\vec{r}',\omega) \\ &\left(\frac{\langle\Psi_n^0|\,\hat{n}(\vec{r}')\,|\Psi_0^0\rangle\,\langle\Psi_0^0|\,\hat{n}(\vec{r})\,|\Psi_n^0\rangle}{\omega_{n0}-\tilde{\omega}} + \frac{\langle\Psi_0^0|\,\hat{n}(\vec{r}')\,|\Psi_n^0\rangle\,\langle\Psi_n^0|\,\hat{n}(\vec{r})\,|\Psi_0^0\rangle}{\omega_{n0}+\tilde{\omega}}\right).\end{aligned} \tag{65}$$

A change of variables $\omega \to -\omega$ was used in the second term in the above expression, leaving the intgeral $\int_{-\infty}^{\infty} d\omega$ invariant. In addition, it was used that the change in the external potential $\delta v_{ext}(\vec{r},t)$ is a real function. For the Fourier transformation of a real function $f(t)$, the following identity holds:

$$\mathcal{F}[f(t)](\omega)^* = \mathcal{F}[f(t)](-\omega). \tag{66}$$

The density change in frequency space is easily obtained by noticing that equation (65) is a Fourier transform from the frequency domain to the time domain. Omitting the integration and just writing down the integrand yields the density change in frequency space:

$$\begin{aligned}\delta n(\vec{r},\omega) = &-\sum_{n\neq 0}\int d^3\vec{r}'\,\delta v_{ext}(\vec{r}',\omega) \\ &\left(\frac{\langle\Psi_n^0|\,\hat{n}(\vec{r}')\,|\Psi_0^0\rangle\,\langle\Psi_0^0|\,\hat{n}(\vec{r})\,|\Psi_n^0\rangle}{\omega_{n0}-\tilde{\omega}} + \frac{\langle\Psi_0^0|\,\hat{n}(\vec{r}')\,|\Psi_n^0\rangle\,\langle\Psi_n^0|\,\hat{n}(\vec{r})\,|\Psi_0^0\rangle}{\omega_{n0}+\tilde{\omega}}\right).\end{aligned} \tag{67}$$

In this step, the limit $\eta \to 0$ has been performed such that $\tilde{\omega}$ turns into ω.
The response function of a system is defined to be the change of the electron density of the system with respect to a change in the external potential acting on that system, as defined in equation (35). Therefore, taking the functional derivative of the change of density in frequency space yields the response function in frequency space:

$$\chi(\vec{r},\vec{r}',\omega) = -\sum_{n\neq 0}\left(\frac{\langle\Psi_n^0|\,\hat{n}(\vec{r}')\,|\Psi_0^0\rangle\,\langle\Psi_0^0|\,\hat{n}(\vec{r})\,|\Psi_n^0\rangle}{\omega_{n0}-\tilde{\omega}} + \frac{\langle\Psi_0^0|\,\hat{n}(\vec{r}')\,|\Psi_n^0\rangle\,\langle\Psi_n^0|\,\hat{n}(\vec{r})\,|\Psi_0^0\rangle\,.}{\omega_{n0}+\tilde{\omega}}\right) \tag{68}$$

Equation (68) is the general form of the response function due to a change in the external potential. As mentioned before it is important to calculate the response function of the Kohn Sham system first in order to determine the response function of the interacting system as they are connected via Dyson's equation (42).
Consider now the Kohn-Sham system, in which the electrons aren't interacting with each other but are moving in an effective external potential. The ground state of such an N-particle system can be written as a Slater determinant of the first N occupied single particle states $|\Psi_i\rangle$. For simplicity, the antisymmetrization for a fermionic system is neglected, and only a Hartree product is considered. The ground state wavefunction then takes the form:

$$\Psi_0^0(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2)...\Psi_a(\vec{r}_i)...\Psi_N(\vec{r}_N). \tag{69}$$

In this formalism, an excited state can be constructed by moving the i-th electron ($i \in \{1, ...N\}$) from one of the first N occupied states to an unoccupied state. Such an excited state is written as

$$\Psi_n^0(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = \Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2)...\Psi_b(\vec{r}_i)...\Psi_N(\vec{r}_N) \tag{70}$$

for some b with $b \geq N$.
The notation here can be somewhat misleading. In equation (69), $\Psi_a(\vec{r}_i)$ means that the i-th electron is currently in the state Ψ_a with energy E_a^0, which is one of the states with the N lowest eigenenergies. In equation (70), the same particle has been moved from state Ψ_a into state Ψ_b with eigenenergy $E_b^0 > E_a^0$. Ψ_b isn't part of the first N states, which is why the total energy of the system is now greater than in the groundstate.
In order to calculate the response function for the Kohn-Sham system, one first needs to evaluate the products $\langle\Psi_0^0|\,\hat{n}(\vec{r})\,|\Psi_n^0\rangle$ appearing in (68).

$$\begin{aligned}
\langle\Psi_0^0|\,\hat{n}(\vec{r})\,|\Psi_n^0\rangle &= \sum_{k=1}^{N} \int d^3\vec{r}_1...d^3\vec{r}_N \Psi_1(\vec{r}_1)^*...\Psi_a(\vec{r}_i)^*...\Psi_N(\vec{r}_N)^*\delta^{(3)}(\vec{r}-\vec{r}_k) \\
&\qquad \Psi_1(\vec{r}_1)...\Psi_b(\vec{r}_i)...\Psi_N(\vec{r}_N) \\
&= \sum_{k=1,k\neq i}^{N} \Psi_k(\vec{r})^*\Psi_k(\vec{r}) \int d^3\vec{r}_1...d^3\vec{r}_{k-1}d^3\vec{r}_{k+1}...d^3\vec{r}_i...d^3\vec{r}_N \\
&\quad \Psi_1(\vec{r}_1)^*...\Psi_a(\vec{r}_i)^*...\Psi_{k-1}(\vec{r}_{k-1})^*\Psi_{k+1}(\vec{r}_{k+1})^*...\Psi_N(\vec{r}_N)^* \\
&\quad \Psi_1(\vec{r}_1)...\Psi_b(\vec{r}_i)...\Psi_{k-1}(\vec{r}_{k-1})\Psi_{k+1}(\vec{r}_{k+1})...\Psi_N(\vec{r}_N) \\
&\quad + \int d^3\vec{r}_i\delta^3(\vec{r}-\vec{r}_i)\Psi_a(\vec{r}_i)^*\Psi_b(\vec{r}_i) = \Psi_a(\vec{r})^*\Psi_b(\vec{r}).
\end{aligned} \tag{71}$$

Each term in the sum contains a scalar product $\langle\Psi_a|\Psi_b\rangle$ when the integration over $d^3\vec{r}_i$ is evaluated. Due to the orthonormality of eigenstates of the Hamiltonian, all of these terms vanish. Only the term in the summation for $k = i$ remains.
Up to this point, only excited states, where one electron is moved from an occupied to an unoccupied state, were considered. Obviously, moving two or even more electrons out of their original states also yields an excited state. However, the contribution of these excited states to the product $\langle\Psi_0^0|\,\hat{n}(\vec{r})\,|\Psi_n^0\rangle$ is null because $n(\vec{r})$ is a one particle operator including only a single position operator $\vec{r}$.
For example, consider two electrons switching states, the i-th and the j-th electron. Then the summation in (71) is split up into three seperate sums: $k \neq \{i, j\}, k = i, k = j$. This time, the remaining terms for $k = i$ and $k = j$ will cancel as well since each of them contains a scalar product between an occupied and an unoccupied state. The detailed proof of this fact follows along the same lines as the calculations in equation (71) and will therefore not be repeated.
Plugging this result back into equation (68), the response function in frequency space can be rewritten as:

$$\chi^{KS}(\vec{r},\vec{r}',\omega) = -\sum_{\substack{n\in\\ occ}}\sum_{\substack{m\in\\ unocc}} \left(\frac{\Psi_m(\vec{r}')^*\Psi_n(\vec{r}')\Psi_n(\vec{r})^*\Psi_m(\vec{r})}{\epsilon_m-\epsilon_n-\tilde{\omega}} + \frac{\Psi_n(\vec{r}')^*\Psi_m(\vec{r}')\Psi_n(\vec{r})^*\Psi_m(\vec{r})}{\epsilon_m-\epsilon_n+\tilde{\omega}}\right). \tag{72}$$

The summation over all excited N-particle states is split up into two separate summations over occupied and unoccupied single-particle states as indicated by equation (71). Each excited N-particle state corresponds to a combination of an empty single particle state Ψ_n with $n < N$ and a filled single particle state Ψ_m with $m > N$. In the denominator, the energy differences between two N-particle states are replaced by the energy differences between two single particle energies. This is possible, since only a single electron needs to be moved from an occupied single particle state to an unoccupied state in order to generate an excited N-particle state. It holds that:

$$\omega_{n0} = E_n^0 - E_0^0 = \epsilon_m - \epsilon_n. \tag{73}$$

Within periodic structures, as they exist in a crystal, it is often more convenient to calculate properties of the system in reciprocal space. Therefore, one would like to calculate the Fourier transform $\chi^{KS}(\vec{q},\vec{q}',\omega)$. The Fourier transformed response function will also play an important role in calculating the correlation energy within the RPA.
To do this, it is important to notice that the real response function is invariant under a shift by a lattice vector $\vec{R}$. That means that $\chi(\vec{r}+\vec{R},\vec{r}'+\vec{R},\omega) = \chi(\vec{r},\vec{r}',\omega)$. This

can be understood by realizing that the single particle wavefunction in a periodical structure is a Bloch wave: $\Psi_{n\vec{k}_n}(\vec{r}) = u_n(\vec{r})e^{i\vec{k}_n\cdot\vec{r}}$, where $u_n(\vec{r})$ is a real function with the periodicity of the lattice and $\vec{k}_n$ is the crystal wave vector of the electron. Shifting the arguments $\vec{r}$ and $\vec{r}'$ by $\vec{R}$ in the first argument of equation (72) yields:

$$\begin{aligned}\Psi_m(\vec{r}'+\vec{R})^*\Psi_n(\vec{r}'+\vec{R})\Psi_n(\vec{r}+\vec{R})^*\Psi_m(\vec{r}+\vec{R}) = \\ = e^{-i\vec{k}_m\cdot\vec{R}}\Psi_m(\vec{r}')e^{i\vec{k}_n\cdot\vec{R}}\Psi_n(\vec{r}')e^{-i\vec{k}_n\cdot\vec{R}}\Psi_n^*(\vec{r})e^{i\vec{k}_m\cdot\vec{R}}\Psi_m(\vec{r}).\end{aligned} \tag{74}$$

The phase factors in the equation above all cancel out leaving the response function invariant under a shift by a lattice vector.
This fact has implications for the Fourier transform of the response function $\chi^{KS}(\vec{q},\vec{q}',\omega)$. It results in the two arguments of the response function, $\vec{q}$ and $\vec{q}'$, differing only by a reciprocal lattice vector. To see this, one first writes down the Fourier transform of the response function. The matrix element $\chi(\vec{q},\vec{q}',\omega)$ is obtained by:

$$\begin{aligned}\chi(\vec{q},\vec{q}',\omega) = \langle\vec{q}|\,\hat{\chi}\,|\vec{q}'\rangle = \int d^3\vec{r}d^3\vec{r}'\,\langle\vec{q}|\vec{r}\rangle\,\langle\vec{r}|\,\hat{\chi}\,|\vec{r}'\rangle\,\langle\vec{r}'|\vec{q}'\rangle = \\ \int d^3\vec{r}d^3\vec{r}'\,e^{-i\vec{q}\cdot\vec{r}}e^{i\vec{q}'\cdot\vec{r}'}\,\chi(\vec{r},\vec{r}',\omega).\end{aligned} \tag{75}$$

By using the invariance of χ under a shift by a constant lattice vector $\vec{R}$ and then substituting $\vec{u} = \vec{r}+\vec{R}$ and $\vec{u}' = \vec{r}'+\vec{R}$, the Fourier transform becomes:

$$\chi(\vec{q},\vec{q}',\omega) = e^{i\vec{R}\cdot\left(\vec{q}-\vec{q}'\right)}\int d^3\vec{u}d^3\vec{u}'\,e^{-i\vec{q}\cdot\vec{u}}e^{-i\vec{q}'\cdot\vec{u}'}\,\chi(\vec{u},\vec{u}',\omega) = e^{i\vec{R}\cdot\left(\vec{q}-\vec{q}'\right)}\chi(\vec{q},\vec{q}',\omega). \tag{76}$$

From this equation, it follows that the difference $\vec{q}-\vec{q}'$ is equal to a reciprocal lattice vector $\vec{G}$ in order for the phase factor to equal 1. If that's not the case, equality can only hold for $\chi = 0$. For that reason, the two transformations

$$\vec{q}\to\vec{q}+\vec{G} \quad \text{and} \quad \vec{q}'\to\vec{q}+\vec{G}' \tag{77}$$

are introduced. $\vec{q}$ lies in the first Brillouin zone and $\vec{G}$ and $\vec{G}'$ are two reciprocal lattice vectors. This transformation guarantees that $\vec{q}-\vec{q}' = \vec{G}-\vec{G}'$ is a reciprocal lattice vector.
In addition, by Bloch's theorem the wavefunction of an electron in a periodic potential is a Bloch wave, as mentioned before. The eigenenergies in the denominator of equation (72) will therefore be replaced by the band structure $\epsilon_{m\vec{k}}$.
Then, it only remains to calculate the Fourier transform of the numerator of the fractions in (72). I will present the solution and then show that it is correct:

$$\langle m\vec{k}'|e^{i\left(\vec{q}+\vec{G}\right)\cdot\vec{r}}|n\vec{k}\rangle = \int d^3\vec{r}'\,\Psi^*_{m\vec{k}'}(\vec{r}')e^{i\left(\vec{q}+\vec{G}\right)\cdot\vec{r}'}\,\Psi_{n\vec{k}}(\vec{r}') = \mathscr{F}[\Psi^*_{m\vec{k}'}(\vec{r})\Psi_{n\vec{k}}(\vec{r})] \tag{78}$$

Putting all of the above together and using equation (72) the Fourier transformation of the response function can be written as:

$$\chi^{KS}(\vec{q}+\vec{G},\vec{q}+\vec{G}',i\omega) = -\frac{1}{V}\sum_{\substack{n\vec{k}\in \\ occ}}\sum_{\substack{m\vec{k}'\in \\ uocc}} \frac{\langle\Psi_{m\vec{k}'}|e^{i(\vec{q}+\vec{G})\vec{r}}|\Psi_{n\vec{k}}\rangle\,\langle\Psi_{n\vec{k}}|e^{-i(\vec{q}+\vec{G}')\vec{r}'}|\Psi_{m\vec{k}'}\rangle}{\epsilon_{m\vec{k}'}-\epsilon_{n\vec{k}}-\tilde{\omega}} + \frac{\langle\Psi_{n\vec{k}}|e^{i(\vec{q}+\vec{G})\vec{r}}|\Psi_{m\vec{k}'}\rangle\,\langle\Psi_{m\vec{k}'}|e^{-i(\vec{q}+\vec{G}')\vec{r}'}|\Psi_{n\vec{k}}\rangle}{\epsilon_{m\vec{k}'}-\epsilon_{n\vec{k}}+\tilde{\omega}}. \tag{79}$$

4.2.5 Adiabatic Connection Fluctuation Dissipation Theorem (ACFDT)

This chapter consists of two parts. First, the aforementioned switching parameter λ is introduced. It will provide a smooth transition between the fully interacting Hamiltonian and the Kohn Sham Hamiltonian. It will be shown that the sum of the Hartree energy and the exchange correlation energy E_{Hxc} can be written as an integral over the switching parameter of the expectation value of the interaction part of the Hamiltonian.
In the second part, the linear response function will be used to rewrite the correlation part of E_{xc} into equation (33).
The switching parameter λ will be introduced by defining a set of multiple systems, each governed by a Hamiltonian $\hat{H}(\lambda)$ while λ varies continuously from 0 to 1. The Hamiltonian is then given by

$$\hat{H}(\lambda) = \hat{T} + \hat{V}(\lambda) + \lambda\hat{V}_{ee}. \tag{80}$$

$\hat{V}_{ee}$ is the electron - electron interaction which can be seen in equation (2). $\hat{V}(\lambda) = \sum_{i=1}^{N}\hat{v}_\lambda(\vec{r}_i)$ is the external potential which takes a different form for different choices of λ. Therefore, each choice of λ yields a system in which the particles interact differently strong. However, it is required that the groundstate density of each system takes on the same value as the groundstate density of the fully interacting system. Choosing $\lambda = 0$ leads to the Kohn Sham system while choosing $\lambda = 1$ describes the fully interacting many body system. Its ground state eigenenergy can be written as follows:

$$E = \langle\Psi(1)|\hat{H}(1)|\Psi(1)\rangle = \langle\Psi(1)|\hat{T}+\hat{V}_{ee}|\Psi(1)\rangle + E_{ext}\,, \tag{81}$$

where $|\Psi(1)\rangle$ is the ground state for the fully interacting system.The groundstate of the Kohn Sham system can be written as $|\Psi(0)\rangle$, which is a Slater determinant, an antisymmetric product of single particle states. The external potential is given by $\hat{V}(0) = \sum_{i=1}^{N}\hat{v}_{KS}(\vec{r}_i)$, which is the Kohn Sham potential. The groundstate energy

of the Kohn Sham system can be written as:

$$E = \langle\Psi(0)|\hat{H}(0)|\Psi(0)\rangle = \langle\Psi(0)|\hat{T} + \hat{V}(0)|\Psi(0)\rangle = T_s + E_H + E_{ext} + E_{xc}\,. \quad (82)$$

The Kohn Sham potential energy is again split up into three parts: the classical electrostatic energy (Hartree energy) E_H, the potential energy resulting from the original external potential E_{ext} and the exchange correlation energy E_{xc}.
By combining equation (81) and (82), the sum of the Hartree part and the exchange correlation part can be written as

$$\begin{aligned} E_H + E_{xc} = E - E_{ext} - T_s = \langle\Psi(1)|\hat{H}(1)|\Psi(1)\rangle - \langle\Psi(1)|\hat{V}(1)|\Psi(1)\rangle \\ -(\langle\Psi(0)|\hat{H}(0)|\Psi(0)\rangle - \langle\Psi(0)|\hat{V}(0)|\Psi(0)\rangle), \end{aligned} \quad (83)$$

since

$$E - E_{ext} = \langle\Psi(1)|\hat{H}(1)|\Psi(1)\rangle - \langle\Psi(1)|\hat{V}(1)|\Psi(1)\rangle \quad (84)$$

and

$$T_s = E - (E_H + E_{ext} + E_{xc}) = \langle\Psi(0)|\hat{H}(0)|\Psi(0)\rangle - \langle\Psi(0)|\hat{V}(0)|\Psi(0)\rangle\,. \quad (85)$$

This can be rewritten as:

$$E_H + E_{xc} = \int_0^1 d\lambda \frac{d}{d\lambda}(\langle\Psi(\lambda)|\hat{H}(\lambda)|\Psi(\lambda)\rangle - \langle\Psi(\lambda)|\hat{V}(\lambda)|\Psi(\lambda)\rangle). \quad (86)$$

The integrand in equation (86) can be simplified by using the Hellmann Feynman theorem, which makes a statement about the derivative of the expectation value of an operator that depends continuously on a parameter λ with respect to that parameter. It states that:

$$\frac{d}{d\lambda}\langle\Psi(\lambda)|\hat{H}(\lambda)|\Psi(\lambda)\rangle = \langle\Psi(\lambda)|\frac{d\hat{H}(\lambda)}{d\lambda}|\Psi(\lambda)\rangle\,. \quad (87)$$

The first term then reads:

$$\begin{aligned} \frac{d}{d\lambda}\langle\Psi(\lambda)|\hat{H}(\lambda)|\Psi(\lambda)\rangle = \langle\Psi(\lambda)|\frac{d}{d\lambda}\hat{H}(\lambda)|\Psi(\lambda)\rangle = \\ \langle\Psi(\lambda)|\hat{V}_{ee}|\Psi(\lambda)\rangle + \langle\Psi(\lambda)|\frac{d}{d\lambda}\hat{V}(\lambda)|\Psi(\lambda)\rangle\,. \end{aligned} \quad (88)$$

By requiring that the ground state density remains the same for all λ interacting systems, one can use that $\frac{d}{d\lambda}\langle\Psi(\lambda)|\hat{V}(\lambda)|\Psi(\lambda)\rangle = \langle\Psi(\lambda)|\frac{d}{d\lambda}\hat{V}(\lambda)|\Psi(\lambda)\rangle$. The sum of

the Hartree and exchange correlation energy can then be written as:

$$E_{Hxc} = \int_0^1 d\lambda \, \langle \Psi(\lambda) | \hat{V}_{ee} | \Psi(\lambda) \rangle \, . \tag{89}$$

To obtain the Hartree exchange correlation energy, one therefore has to compute the integral over the switching parameter of the expectation value of the electron electron interaction part of the Hamiltonian.
It isn't straightforward to calculate the expectation value of the electronic interaction operator in the equation above, as the vector $|\Psi(\lambda)\rangle$ is not known. It turns out though that knowledge of the pair density $n^2(\vec{r}_1, \vec{r}_2)$ is enough to evaluate the expectation value of the Coulomb operator.
The expectation value of $\hat{V}_{ee}$ can be calculated as follows:

$$\begin{aligned} \langle \Psi | \hat{V}_{ee} | \Psi \rangle = & \int d^3\vec{r}_1 ... d^3\vec{r}_N d^3\vec{r}^{\,\prime}_1 ... d^3\vec{r}^{\,\prime}_N \\ & \langle \Psi | \vec{r}_1, ... \vec{r}_N \rangle \, \langle \vec{r}_1, ... \vec{r}_N | \hat{V}_{ee} | \vec{r}^{\,\prime}_1, ..., \vec{r}^{\,\prime}_N \rangle \, \langle \vec{r}^{\,\prime}_1, ..., \vec{r}^{\,\prime}_N | \Psi \rangle \, . \end{aligned} \tag{90}$$

In equation (90), the identity operator of the Hilbert space of N particles was inserted twice. As $\hat{V}_{ee}$ is a function solely of position operators, the eigenequation $\hat{V}_{ee} \, |\vec{r}_1, ..., \vec{r}_N\rangle = V_{ee} \, |\vec{r}_1, ..., \vec{r}_N\rangle$ holds. Inserting this relation and using that the position eigenstates form an orthonormal system, the expectation value can be simplified to:

$$\langle \Psi | \, \hat{V}_{ee} \, | \Psi \rangle = \frac{1}{2} \sum_{i \neq j} \int d^3\vec{r}_1 ... d^3\vec{r}_N \Psi^*(\vec{r}_1, ..., \vec{r}_N) \frac{e^2}{\mid \vec{r}_i - \vec{r}_j \mid} \Psi(\vec{r}_1, ..., \vec{r}_N). \tag{91}$$

There are $N(N-1)$ pairs in this sum, all of which yield the same result upon integrating. The expression can therefore be rewritten as:

$$\langle \Psi | \, \hat{V}_{ee} \, | \Psi \rangle = \frac{N(N-1)}{2} \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{e^2}{\mid \vec{r}_1 - \vec{r}_2 \mid} \int d^3\vec{r}_3 ... d^3\vec{r}_N \mid \Psi(\vec{r}_1, ... \vec{r}_n) \mid^2 . \tag{92}$$

By introducing the pair density $n^2(\vec{r}_1, \vec{r}_2) = N(N-1) \int d^3\vec{r}_3 ... d^3\vec{r}_N \mid \Psi(\vec{r}_1, ... \vec{r}_n) \mid^2$, the expectation value takes the form:

$$\langle \Psi | \, \hat{V}_{ee} \, | \Psi \rangle = \frac{e^2}{2} \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{n^2(\vec{r}_1, \vec{r}_2)}{\mid \vec{r}_1 - \vec{r}_2 \mid}. \tag{93}$$

The pair density $n^2(\vec{r}, \vec{r}^{\,\prime})$ describes the probability of finding one electron at position $\vec{r}$ and another electron at position $\vec{r}^{\,\prime}$, independent of the positions of all other electrons. For a state depending on the switching parameter λ, the pair density will also depend on this parameter. Plugging this expression for the expectation value

back into equation (89) yields:

$$E_{Hxc} = \frac{e^2}{2}\int_0^1 d\lambda \int d^3\vec{r}d^3\vec{r}' \frac{n^{2,\lambda}(\vec{r},\vec{r}')}{\mid \vec{r}-\vec{r}' \mid}. \tag{94}$$

In analogy with the density operator for one electron in equation (7), the pair density operator can be written as a sum over products of delta functions:

$$\hat{n}^2(\vec{r},\vec{r}') = \sum_{i\neq j} \delta^{(3)}(\vec{r}-\vec{r}_i)\delta^{(3)}(\vec{r}'-\vec{r}_j). \tag{95}$$

Calculating the expectation value of this operator with respect to an eigenstate of the λ-interacting system $|\Psi(\lambda)\rangle$ yields the pair density of the λ-interacting system.

$$\begin{aligned} n^{2,\lambda}(\vec{r},\vec{r}') &= \langle\Psi(\lambda)|\sum_{i\neq j}\delta^{(3)}(\vec{r}-\vec{r}_i)\delta^{(3)}(\vec{r}'-\vec{r}_j)\,|\Psi(\lambda)\rangle = \\ \langle\Psi(\lambda)|\sum_{i,j}\delta^{(3)}(\vec{r}-\vec{r}_i)\delta^{(3)}(\vec{r}'-\vec{r}_j)\,|\Psi(\lambda)\rangle &- \delta^{(3)}(\vec{r}-\vec{r}')\,\langle\Psi(\lambda)|\sum_i\delta^{(3)}(\vec{r}-\vec{r}_i)\,|\Psi(\lambda)\rangle \\ &= \langle\Psi(\lambda)|\,\hat{n}(\vec{r})\hat{n}(\vec{r}')\,|\Psi(\lambda)\rangle - \delta^{(3)}(\vec{r}-\vec{r}')\,\langle\Psi(\lambda)|\,\hat{n}(\vec{r})\,|\Psi(\lambda)\rangle\,. \end{aligned} \tag{96}$$

From the first to the second row, the sum over all pairs of distinct particles was extended to include pairs of the same particles. Subsequently, this term was subtracted by introducing a counterterm. Additionally, basic identities of the Dirac Delta distribution were used, namely $\delta(\vec{r}-\vec{a})f(\vec{r}) = \delta(\vec{r}-\vec{a})f(\vec{a})$. From the second to the third row, the definition of the density operator for one electron was inserted. In equation (96), the expectation value of a product of single electron density operators appears. In order to evaluate this term, it is helpful to study the following expression:

$$\int_0^\infty d\omega \left(\chi(\vec{r},\vec{r}',i\omega) + \chi(\vec{r}',\vec{r},i\omega)\right). \tag{97}$$

Note that the response functions above have an imaginary frequency argument. From now on, for simplicity, the ground state $|\Psi_0^0\rangle$ will be denoted as $|0\rangle$ and the excited state $|\Psi_n^0\rangle$ as $|n\rangle$. Plugging equation (68) into (97) yields:

$$\begin{aligned} -\sum_{n\neq 0}\int_0^\infty d\omega \,&\frac{\langle n|\,\hat{n}(\vec{r}')\,|0\rangle\,\langle 0|\,\hat{n}(\vec{r})\,|n\rangle}{\omega_{n0}-i\omega-i\eta} + \frac{\langle 0|\,\hat{n}(\vec{r}')\,|n\rangle\,\langle n|\,\hat{n}(\vec{r})\,|0\rangle}{\omega_{n0}+i\omega+i\eta} \\ &+ \frac{\langle n|\,\hat{n}(\vec{r})\,|0\rangle\,\langle 0|\,\hat{n}(\vec{r}')\,|n\rangle}{\omega_{n0}-i\omega-i\eta} + \frac{\langle 0|\,\hat{n}(\vec{r})\,|n\rangle\,\langle n|\,\hat{n}(\vec{r}')\,|0\rangle}{\omega_{n0}+i\omega+i\eta}. \end{aligned} \tag{98}$$

The integrand can be factored to yield:

$$- \sum_{n \neq 0} \left(\langle 0| \hat{n}(\vec{r}) |N\rangle \langle N| \hat{n}(\vec{r}') |0\rangle + \langle 0| \hat{n}(\vec{r}') |N\rangle \langle N| \hat{n}(\vec{r}) |0\rangle \right) \left(\frac{1}{\omega_{n0} - i\omega - i\eta} + \frac{1}{\omega_{n0} + i\omega + i\eta} \right). \tag{99}$$

In the next step, the ω integration can be carried out. The braket products are independent of ω and can therefore be ignored for now:

$$\int_0^\infty d\omega \left(\frac{1}{\omega_{n0} - i\omega - i\eta} + \frac{1}{\omega_{n0} + i\omega + i\eta} \right) = \int_0^\infty d\omega \frac{2\omega_{n0}}{\omega_{n0}^2 + (\omega + \eta)^2} = \frac{2}{\omega_{n0}} \int_0^\infty d\omega \frac{1}{1 + \left(\frac{\omega+\eta}{\omega_{n0}}\right)^2} = \frac{2}{\omega_{n0}} \int_{\frac{\eta}{\omega_{n0}}}^\infty d\omega\, \omega_{n0} \frac{1}{1 + \omega'^2} = 2arctan\left(\omega'\right) \Big|_{\frac{\eta}{\omega_{n0}}}^\infty = \pi \tag{100}$$

In the last line, the limit $\eta \to 0$ was performed.
Using this, the expression in equation (97) can be written as:

$$\begin{aligned} \int_0^\infty d\omega \left(\chi(\vec{r}, \vec{r}', i\omega) + \chi(\vec{r}', \vec{r}, i\omega) \right) &= -\pi \sum_{n \neq 0} \left(\langle 0| \hat{n}(\vec{r}) |n\rangle \langle n| \hat{n}(\vec{r}') |0\rangle + \langle 0| \hat{n}(\vec{r}') |n\rangle \langle n| \hat{n}(\vec{r}) |0\rangle \right) \\ &= -\pi \sum_{n} \left(\langle 0| \hat{n}(\vec{r}) |n\rangle \langle n| \hat{n}(\vec{r}') |0\rangle + \langle 0| \hat{n}(\vec{r}') |n\rangle \langle n| \hat{n}(\vec{r}) |0\rangle \right) \\ &\quad + \pi \langle 0| \hat{n}(\vec{r}) |0\rangle \langle 0| \hat{n}(\vec{r}') |0\rangle + \langle 0| \hat{n}(\vec{r}') |0\rangle \langle 0| \hat{n}(\vec{r}) |0\rangle . \end{aligned} \tag{101}$$

In the second line of the above expression, the zeroth term in the summation was both added and subtracted, hence the index in the summation does not exclude $n = 0$ anymore. As the set of eigenvectors of the unperturbed Hamiltonian $\{|n\rangle$ is a complete set of orthonormal states, we can use the completeness relation $\sum_n |n\rangle \langle n| = 1$. Equation (97) can then be simplified to:

$$\int_0^\infty d\omega \left(\chi(\vec{r}, \vec{r}', i\omega) + \chi(\vec{r}', \vec{r}, i\omega) \right) = -\pi \left(\langle 0| \hat{n}(\vec{r}) \hat{n}(\vec{r}') |0\rangle + \langle 0| \hat{n}(\vec{r}') \hat{n}(\vec{r}) |0\rangle \right) + 2\pi n(\vec{r}) n(\vec{r}'). \tag{102}$$

The response function used up to this point in the calculation above was the one of a non interacting system of electrons. However, the derived formula is also valid in the general case of an interacting system. To describe such a system, one needs to make the following replacements by using the switching parameter λ:
First, $|\Psi_0^0\rangle = |0\rangle \to |\Psi(\lambda)\rangle$, where $|\Psi(\lambda)\rangle$ is the ground state of the λ-interacting system. Secondly, the response function of the Kohn-Sham system will be replaced

by the response function of the λ-interacting system χ^λ.
An expression for the pair density was already derived in equation (96). Plugging this result into the formula for the Hartree exchange correlation energy (94) yields:

$$E_{Hxc} = \frac{e^2}{2}\int_0^1 d\lambda \int d^3\vec{r}d^3\vec{r}' \frac{1}{\mid \vec{r}-\vec{r}' \mid}\left(\langle\Psi(\lambda)|\,\hat{n}(\vec{r})\hat{n}(\vec{r}')\,|\Psi(\lambda)\rangle - \delta^{(3)}(\vec{r}-\vec{r}')n(\vec{r})\right). \tag{103}$$

In the next step, the product $n(\vec{r})n(\vec{r}')$ is being symmetrised. That means it is being replaced by $\frac{1}{2}(n(\vec{r})n(\vec{r}')+n(\vec{r}')n(\vec{r}))$. This is possible, since renaming the integration variables and then switching the order of integration in the second summand yields the same result as leaving the first summand indifferent. Additionally, the Coulomb potential $\frac{1}{|\vec{r}-\vec{r}'|}$ stays invariant when $\vec{r}$ and $\vec{r}'$ are being interchanged. Equation (103) can then be rewritten as:

$$\begin{aligned} E_{Hxc} = \frac{e^2}{2}\int_0^1 d\lambda \int d^3\vec{r}d^3\vec{r}' \frac{1}{\mid \vec{r}-\vec{r}' \mid} \\ \left(\langle\Psi(\lambda)|\,\frac{1}{2}\left(\hat{n}(\vec{r})\hat{n}(\vec{r}')+n(\vec{r})n(\vec{r}')\right)|\Psi(\lambda)\rangle - \delta^{(3)}(\vec{r}-\vec{r}')n(\vec{r})\right). \end{aligned} \tag{104}$$

This is where the auxiliary calculation from before comes into play, as the expectation value of $\frac{1}{2}(\hat{n}(\vec{r})\hat{n}(\vec{r}')+\hat{n}(\vec{r}')\hat{n}(\vec{r}))$ with respect to the groundstate of the λ interacting system has been calculated in equation (102). Rearranging terms and plugging into the equation above leads to:

$$\begin{aligned} E_{Hxc} = \frac{e^2}{2}\int_0^1 d\lambda \int d^3\vec{r}d^3\vec{r}' \frac{1}{\mid \vec{r}-\vec{r}' \mid} \\ \frac{1}{2}\left(-\frac{1}{\pi}\int d\omega\left(\chi^\lambda(\vec{r},\vec{r}',i\omega)+\chi^\lambda(\vec{r}',\vec{r},i\omega)\right)+2n(\vec{r})n(\vec{r}')\right) - \delta^{(3)}(\vec{r}-\vec{r}')n(\vec{r}). \end{aligned} \tag{105}$$

Now, the same symmetrisation trick as before is applied, just in the other direction. One notices that the integration over $\chi^\lambda(\vec{r},\vec{r}',i\omega)$ will yield the same result as the integration over $\chi^\lambda(\vec{r}',\vec{r},i\omega)$. Therefore, only the first term is kept and multiplied by 2. The Hartree exchange correlation energy is then finally given by:

$$\begin{aligned} E_{Hxc} = \frac{e^2}{2}\int_0^1 d\lambda \int d^3\vec{r}d^3\vec{r}' \frac{1}{\mid \vec{r}-\vec{r}' \mid} \\ \left(n(\vec{r})n(\vec{r}') - \frac{1}{\pi}\int d\omega\chi^\lambda(\vec{r},\vec{r}',i\omega) - \delta^{(3)}(\vec{r}-\vec{r}')n(\vec{r})\right). \end{aligned} \tag{106}$$

The first summand corresponds precisely to the classical Hartree energy, as explained by equation (86). After neglecting the Hartree energy, only the exchange-correlation energy remains:

$$E_{xc} = -\frac{e^2}{2}\int_0^1 d\lambda \int d^3\vec{r}d^3\vec{r}' \frac{1}{\mid \vec{r}-\vec{r}' \mid}\left(\frac{1}{\pi}\int_0^\infty d\omega \chi^\lambda(\vec{r},\vec{r}',i\omega) + n(\vec{r})\delta^3(\vec{r}-\vec{r}')\right). \tag{107}$$

In order to further simplify this expression, consider the integrand only for $\lambda = 0$. The first summand of the integrand then takes the form:

$$-\frac{e^2}{2}\int d^3\vec{r}d^3\vec{r}' \frac{1}{\mid \vec{r}-\vec{r}' \mid}\frac{1}{\pi}\int_0^\infty d\omega \chi^{KS}(\vec{r},\vec{r}',i\omega). \tag{108}$$

In order to rewrite this expression one makes use of equations (97) and (71) and applies the same trick as before. At first, the frequency integration over χ^{KS} is being symmetrised. The integrand then takes the form:

$$\begin{aligned}\int_0^\infty d\omega \left(\chi^{KS}(\vec{r},\vec{r}',i\omega) + \chi^{KS}(\vec{r}',\vec{r},i\omega)\right) = \\ -\pi \sum_{\substack{n\in\\ occ}}\sum_{\substack{m\in\\ unocc}} \left(\Psi_n^*(\vec{r})\Psi_m(\vec{r})\Psi_n(\vec{r}')\Psi_m^*(\vec{r}') + \Psi_n(\vec{r})\Psi_m^*(\vec{r})\Psi_n^*(\vec{r}')\Psi_m(\vec{r}')\right).\end{aligned} \tag{109}$$

Interchanging integration variables and then switching the order of integration in one of the two sums shows that both terms yield the same contribution when intergrated. Plugging this result back into equation (108), the π's and the minus sign cancel, leaving:

$$\frac{e^2}{2}\sum_{\substack{n\in\\ occ}}\sum_{\substack{m\in\\ unocc}} 2\int d^3\vec{r}d^3\vec{r}' \frac{\Psi_n^*(\vec{r})\Psi_m(\vec{r})\Psi_n(\vec{r}')\Psi_m^*(\vec{r}')}{\mid \vec{r}-\vec{r}' \mid}. \tag{110}$$

The expression in the second summand can be replaced by inserting the following two expressions: $\delta^3(\vec{r}-\vec{r}') = \sum_m \Psi_m^*(\vec{r}')\Psi_m(\vec{r})$ and $n(\vec{r}) = 2\sum_{\substack{n\in\\ occ}} \Psi_n^*(\vec{r})\Psi_n(\vec{r})$. Note that the first summation runs over all single particle states, while the second sum runs only over those states that are occupied in the groundstate. This yields:

$$-\frac{e^2}{2}\int d^3\vec{r}d^3\vec{r}' \frac{n(\vec{r})\delta^{(3)}(\vec{r}-\vec{r}')}{\mid \vec{r}-\vec{r}' \mid} = -\frac{e^2}{2}\sum_{\substack{n\in\\ occ}}\sum_m 2\int d^3\vec{r}d^3\vec{r}' \frac{\Psi_m^*(\vec{r}')\Psi_n(\vec{r}')\Psi_n^*(\vec{r})\Psi_m(\vec{r})}{\mid \vec{r}-\vec{r}' \mid}. \tag{111}$$

Note again that the summation indices m and n in the above equation run over a

different set of single particle wave functions. When plugging both these expressions, namely (110) and (111) back into the exchange correlation energy for $\lambda = 0$ in equation (108), one needs to subtract all unoccupied states from the entirety of all states, leaving only the occupied states behind. This yields:

$$E_{xc} \mid_{\lambda=0} = -\frac{e^2}{2} \sum_{\substack{n\in \\ occ}} \sum_{\substack{m\in \\ occ}} 2 \int d^3\vec{r} d^3\vec{r}' \, \frac{\Psi_m^*(\vec{r}')\Psi_n(\vec{r}')\Psi_n^*(\vec{r})\Psi_m(\vec{r})}{\mid \vec{r} - \vec{r}' \mid} := E_x[\{\Psi^{KS}\}]. \quad (112)$$

For $\lambda = 0$, the exchange correlation energy only has a contribution from the exchange part. It is a functional of the Kohn Sham orbitals $\{\Psi^{KS}\}$. The next step is to split up the exchange correlation energy into two parts: The exchange energy E_x, which has already been found and the correlation energy E_c.
The exchange energy has been calculated separately for $\lambda = 0$ and thus needs to be subtracted again from E_{xc}. Using the result derived in (112), the exchange correlation energy can therefore be written as:

$$\begin{aligned} E_{xc} = E_x[\{\Psi^{KS}\}] - \frac{e^2}{2} \int_0^1 d\lambda \int d^3\vec{r} d^3\vec{r}' \, \frac{1}{\mid \vec{r} - \vec{r}' \mid} \\ \frac{1}{\pi} \int d\omega \left(\chi^\lambda(\vec{r}, \vec{r}', i\omega) - \chi^{KS}(\vec{r}, \vec{r}', i\omega) \right). \end{aligned} \quad (113)$$

Equation (113) is of the desired form $E_{xc} = E_x + E_c$. Thus, the correlation energy is given by:

$$E_c = -\int_0^1 d\lambda \int d^3\vec{r} d^3\vec{r}' \, \frac{e^2}{\mid \vec{r} - \vec{r}' \mid} \int_0^\infty \frac{d\omega}{2\pi} \left(\chi^\lambda(\vec{r}, \vec{r}', i\omega) - \chi^{KS}(\vec{r}, \vec{r}', i\omega) \right). \quad (114)$$

All contributions to the exchange correlation energy from interacting systems, i.e. $\lambda \neq 0$, are included in the correlation energy, while all effects of a non interacting Kohn Sham system are included in the exchange part. Therefore, in the following, the focus will be on the correlation energy which contains the information about the interacting system.
In theory, equation (114) is an exact formula for the correlation energy. However one usually does not have full knowledge of the response function of the λ-interacting system χ^λ, only the Kohn Sham response function χ^{KS}. Within the RPA, it is possible to derive an expression for E_c that depends solely on χ^{KS}. The connection between the two response functions is given by Dyson's equation (42), where the response function of the fully interacting system χ is replaced by χ^λ:

$$\chi^{\lambda}(\vec{r},\vec{r}',\omega) = \chi^{KS}(\vec{r},\vec{r}',\omega) + \int d^3\vec{r}_1 d^3\vec{r}_2 \chi^{KS}(\vec{r},\vec{r}_1,\omega)\left(\frac{e^2\lambda}{\mid \vec{r}_1 - \vec{r}_2 \mid} + f_{xc}^{\lambda}(\vec{r}_1,\vec{r}_2,\omega)\right)\chi(\vec{r}_2,\vec{r}',\omega). \tag{115}$$

In order to derive the expression for the correlation energy within the RPA, the last two equations need to be converted to reciprocal space first. The response function $\chi^{\lambda}(\vec{r},\vec{r}',i\omega)$ becomes $\chi^{\lambda}(\vec{q}+\vec{G},\vec{q}+\vec{G}',i\omega)$,the Coulomb potential becomes $v(\vec{q}+\vec{G},\vec{q}+\vec{G}') = \frac{4\pi e^2}{|\vec{q}+\vec{G}|^2}\delta_{\vec{G},\vec{G}'}$ and the integration $\int d^3\vec{r}d^3\vec{r}'$ becomes a summation $\sum_{\vec{q}\in BZ}\sum_{\vec{G},\vec{G}'}$. After eliminating one of the summations by using the delta function in the Coulomb potential, the correlation energy can then be rewritten in reciprocal space as:

$$E_c = -\int_0^1 d\lambda \int_0^{\infty}\frac{d\omega}{2\pi}\sum_{\vec{q}\in BZ}\sum_{\vec{G}}\frac{4\pi e^2}{\mid \vec{q}+\vec{G} \mid^2}\left(\chi^{\lambda}(\vec{q}+\vec{G},\vec{q}+\vec{G},i\omega) - \chi^{KS}(\vec{q}+\vec{G},\vec{q}+\vec{G},i\omega)\right). \tag{116}$$

Defining the trace of two functions in reciprocal space by

$$Tr(AB) = \sum_{\vec{q}\in BZ}\sum_{\vec{G},\vec{G}'} A(\vec{q}+\vec{G},\vec{q}+\vec{G}')B(\vec{q}+\vec{G}',\vec{q}+\vec{G}), \tag{117}$$

the correlation energy becomes:

$$E_c = -\int_0^1 d\lambda \int_0^{\infty}\frac{d\omega}{2\pi} Tr\left(v\left(\chi^{\lambda}(i\omega) - \chi^{KS}(i\omega)\right)\right). \tag{118}$$

For brevity, the dependencies of the response functions on the reciprocal lattice vectors have been omitted. Converting Dyson's equation (115) into reciprocal space and using the shorthand notation $\chi^{\lambda}_{\vec{G},\vec{G}'}(\vec{q},i\omega) = \chi^{\lambda}(\vec{q}+\vec{G},\vec{q}+\vec{G},i\omega)$ for the response function then reads:

$$\chi^{\lambda}_{\vec{G},\vec{G}'}(\vec{q},i\omega) = \chi^{KS}_{\vec{G},\vec{G}'}(\vec{q},i\omega) + \sum_{\vec{G}_1,\vec{G}_2}\chi^{KS}_{\vec{G},\vec{G}_1}(\vec{q},i\omega)\left(\frac{4\pi e^2\lambda}{\mid \vec{q}+\vec{G}_1 \mid^2}\delta_{\vec{G}_1,\vec{G}_2} + f^{\lambda}_{xc,\vec{G}_1,\vec{G}_2}(\vec{q},i\omega)\right)\chi^{\lambda}_{\vec{G}_2,\vec{G}'}(\vec{q},i\omega). \tag{119}$$

The better the approximation of the exchange correlation kernel f_{xc}, the better the result for χ^{λ} will be. In the random phase approximation one sets the exchange correlation kernel to be 0. Dyson's equation then becomes:

$$\chi^{\lambda}_{\vec{G},\vec{G}'}(\vec{q},i\omega) = \chi^{KS}_{\vec{G},\vec{G}'}(\vec{q},i\omega) + \sum_{\vec{G}_1,\vec{G}_2}\chi^{KS}_{\vec{G},\vec{G}_1}(\vec{q},i\omega)\frac{4\pi e^2\lambda}{\mid \vec{q}+\vec{G}_1 \mid^2}\delta_{\vec{G}_1,\vec{G}_2}\chi^{\lambda}_{\vec{G}_2,\vec{G}'}(\vec{q},i\omega) \tag{120}$$

Using the convergence theorem for the geometric series, that is $\sum_{k=0}^{\infty} x^k = \frac{1}{1-x}$ for $\mid x \mid < 1$, and plugging in $\lambda\chi^{KS}_{\vec{G},\vec{G}'}(\vec{q}, i\omega)v$ for x, the expression above for the response function can be written as

$$\chi^{\lambda}_{\vec{G},\vec{G}'}(\vec{q}, i\omega) = \sum_{\vec{G}''} \Big(1 - \lambda\chi^{KS}(\vec{q}, i\omega)v\Big)^{-1}_{\vec{G},\vec{G}''} \chi^{KS}_{\vec{G}'',\vec{G}'}(\vec{q}, i\omega). \tag{121}$$

Another trick that can be used to further simplify the expression for the correlation energy in equation (118) is to insert the following identity:

$$Tr(v\chi^{\lambda}) = -\frac{\partial}{\partial\lambda} Tr(\ln\Big(1 - \lambda\chi^{KS}v\Big)). \tag{122}$$

In order to prove this identity, one first writes out the definition of the trace in reciprocal space and then takes the derivative with respect to λ by using the chain rule:

$$-\frac{\partial}{\partial\lambda}\sum_{\vec{G}} ln(1 - \lambda\chi^{KS}v)_{\vec{G},\vec{G}} = \sum_{\vec{G},\vec{G}_1,\vec{G}_2} (1 - \lambda\chi^{KS}v)^{-1}_{\vec{G},\vec{G}_1}\chi^{KS}_{\vec{G}_1,\vec{G}_2} v_{\vec{G}_2,\vec{G}}. \tag{123}$$

Here, $\ln\Big(1 - \lambda\chi^{KS}v\Big)_{\vec{G},\vec{G}}$ is obtained by first calculating the logarithm of the matrix $1 - \lambda\chi^{KS}$ and then taking the $\vec{G},\vec{G}$-th element of the resulting matrix.
The reciprocal Coulomb potential $v_{\vec{G}_2,\vec{G}}$ is proportional to the Kronecker delta $\delta_{\vec{G}_2,\vec{G}}$. Using this and the expression for the response function of the λ-interacting system (121), the derivative can be further simplified to yield the desired result:

$$\sum_{\vec{G},\vec{G}_1} (1 - \lambda\chi^{KS}v)^{-1}_{\vec{G},\vec{G}_1}\chi^{KS}_{\vec{G}_1,\vec{G}} v_{\vec{G},\vec{G}} = \sum_{\vec{G}} \chi^{\lambda}_{\vec{G},\vec{G}} v_{\vec{G},\vec{G}} = Tr(\chi^{\lambda}v). \tag{124}$$

Using this identity, the λ-integration in the first summand of the correlation energy in equation (118) cancels with the partial derivative:

$$-\int_0^1 d\lambda Tr(v\chi^{\lambda}) = \int_0^1 d\lambda \left(-\frac{\partial}{\partial\lambda} Tr(\ln\Big(1 - \lambda\chi^{KS}v\Big))\right) = Tr(\ln\Big(1 - \chi^{KS}v\Big)). \tag{125}$$

As the second summand in the correlation energy is λ-independent, the integration only adds a multiplicative factor of 1 after evaluation and can therefore be omitted entirely. The final formula for the RPA correlation energy then reads:

$$E_c = \int_0^{\infty} \frac{d\omega}{2\pi} Tr(ln(1 - \chi^{KS}v) + \chi^{KS}v). \tag{126}$$

5 Implementation

5.1 Introduction

This chapter provides a review of the interpolation procedure that was performed during this Master's thesis. The first two chapters are dedicated to two necessary mathematical preliminaries. At first, the expression for the RPA correlation energy in equation (126) will be rewritten which will be helpful for the subsequent interpolation in VASP. Second, the algorithm for the cubic spline interpolation implemented in VASP will be presented.
One section is dedicated to the procedure that was used to calculate the RPA correlation energy in VASP. The necessary scripts to perform these calculations are supplemented in the appendix. The final two sections explain the implementation of the tricubic spline interpolation in VASP in detail. The functionality of the central routines and variables is explained.

5.2 Definition of the electronic structure factor

For the purpuse of this thesis, it is necessary to rewrite the expression for the correlation energy in the RPA, which was derived in the previous section. The goal is to find a function $S(\vec{q}+\vec{G},\vec{q}+\vec{G}')$, called the electronic structure factor, such that E_c can be written as:

$$E_c = \mathrm{Tr}\,(vS)\,, \tag{127}$$

where Tr is defined in equation (117). One starts from the expression of the correlation energy for the RPA within the ACFDT approach:

$$E_c = \frac{1}{2\pi}\int_0^\infty d\omega\, Tr(\ln\Big(1-\chi^{KS}v\Big)+\chi^{KS}v). \tag{128}$$

The only frequency dependent part here is the Kohn Sham response function χ^{KS}. However, for now, the frequency integration will be neglected and the focus will be only on the integrand. For brevity, χ^{KS} will be replaced by χ.
One uses the Taylor expansion for $\ln(1-x) = -\sum_{n=1}^{\infty}\frac{x^n}{n}$ to expand the Trace within equation (128):

$$Tr(\ln(1-\chi v)+\chi v) = Tr(-\chi v - \frac{1}{2}(\chi v)^2 - \frac{1}{3}(\chi v)^3 ... + \chi v). \tag{129}$$

The first and last term cancel and one obtains

$$Tr(-\frac{1}{2}(\chi v)^2 - \frac{1}{3}(\chi v)^3 - ...)\,. \tag{130}$$

From now on, it will be more convenient to replace the product χv by its symmetric product $v^{\frac{1}{2}}\chi v^{\frac{1}{2}}$. This doesn't change the trace and has the benefit that $v^{\frac{1}{2}}\chi v^{\frac{1}{2}}$ is a Hermitian matrix. Hermitian matrices are always diagonalizable having real eigenvalues. This leads to:

$$Tr((-\frac{1}{2}(v^{\frac{1}{2}}\chi v^{\frac{1}{2}})^2 - \frac{1}{3}(v^{\frac{1}{2}}\chi v^{\frac{1}{2}})^3 - ...)). \tag{131}$$

In the previuos step, it was used that the trace function is invariant under cyclic permutations of its arguments, which means that:

$$Tr\left(ABC\right) = Tr\left(CAB\right). \tag{132}$$

The trace expression above can now be rewritten again in a compact form as a logarithm:

$$Tr\left(ln\left(1 - v^{\frac{1}{2}}\chi v^{\frac{1}{2}}\right) + v^{\frac{1}{2}}\chi v^{\frac{1}{2}}\right). \tag{133}$$

In the next step, the factor 1 is inserted by multiplying with $v^{-\frac{1}{2}}vv^{-\frac{1}{2}}$. Using again the cyclic permutation property, the expression takes the form:

$$Tr\left(vv^{-\frac{1}{2}}\left(ln\left(1 - v^{\frac{1}{2}}\chi v^{\frac{1}{2}}\right) + v^{\frac{1}{2}}\chi v^{\frac{1}{2}}\right)v^{-\frac{1}{2}}\right). \tag{134}$$

At this point, the function $\hat{S}$ can be defined as:

$$\hat{S} \coloneqq v^{-\frac{1}{2}}\left(ln\left(1 - v^{\frac{1}{2}}\chi v^{\frac{1}{2}}\right) + v^{\frac{1}{2}}\chi v^{\frac{1}{2}}\right)v^{-\frac{1}{2}}. \tag{135}$$

$\hat{S}(\vec{q}+\vec{G}, \vec{q}+\vec{G}')$ is therefore a matrix, just as χ in equation (79). Each entry is determined by two vectors $\vec{q}+\vec{G}$ and $\vec{q}+\vec{G}'$. Inserting all this back into equation (126), the correlation energy can be written as:

$$E_c = \int_0^\infty \frac{d\omega}{2\pi} Tr\left(v\hat{S}\right). \tag{136}$$

In VASP, the frequency integration is carried out before the evaluation of the trace function. Therefore, the frequency dependency in $\hat{S}$ is integrated over, defining a new function $S = \int_0^\infty d\omega \hat{S}$, the electronic structure factor. The correlation energy can thus be written as:

$$E_c = Tr\left(vS\right) = \sum_{\vec{q}+\vec{G}} v(\vec{q}+\vec{G})S(\vec{q}+\vec{G}). \tag{137}$$

In this equation, the short notation of $S(\vec{q}+\vec{G})$ stands for the diagonal elements

of the structure factor $S(\vec{q}+\vec{G},\vec{q}+\vec{G})$. They are the only elements of S which are included in the trace function, since the Coulomb kernel is diagonal in reciprocal space.

5.3 Natural cubic spline interpolation

Cubic spline interpolation is a special form of interpolation, in which the interpolating function is a piecewise polynomial of third degree which is twice continuously differentiable [12] [13]. There exist different approaches to determine the interpolation polynomial, we will largely follow [14].
Suppose that an interval $[a,b]$ is given on the real line and that there are $n+1$ given points within that interval that can be ordered in the following way: $a = x_0 < x_1 < ... < x_{n-1} < x_n = b$. The values of some function $y(x)$, which is not known analytically, are known at these points exclusively as well. They will be denoted by $y_0 = y(x_0)$, $y_1 = y(x_1)$ and so on.
The goal is to find a piecewise defined polynomial $P(x)$ to approximate the function $y(x)$ in the interval $[a,b]$. To do this, one begins with defining the n subintervals of $[a,b]$ originating from splitting up $[a,b]$ into n parts:

$$I_i = [x_i, x_{i+1}] \quad \text{for} \quad i = 0, ..., n-1. \tag{138}$$

For each of these intervals, one defines a polynomial of third degree:

$$P_i(x) = a_i + b_i(x-x_i) + c_i(x-x_i)^2 + d_i(x-x_i)^3 \quad \text{for} \quad i = 0, ..., n-1. \tag{139}$$

Each of these polynomials $P_i(x)$ is only defined for $x \in I_i$. The interpolating polynomial $P(x)$ is then generated by stringing together all the polynomials $P_i(x)$ for $i = 0, ...n-1$

$$P(x) = \left\{ \begin{array}{ll} P_0(x), & \text{for } x \in I_0 \\ P_1(x), & \text{for } x \in I_1 \\ . & \\ . & \\ P_{n-2}(x), & \text{for } x \in I_{n-2} \\ P_{n-1}(x), & \text{for } x \in I_{n-1} \end{array} \right\}.$$

There are n intervals in total, with each interval requiring 4 coefficients a, b, c, d in order to fully define the interpolating polynomial $P_i(x)$. This makes for $4n$ unknown coefficients. They can be found by requiring certain properties of the piecewise

polynomials. First of all, the values of the piecewise polynomials have to match the known values of the function on each subinterval. Mathematically formulated, this means $P_i(x_i) = y_i \quad \text{and} \quad P_i(x_{i+1}) = y_{i+1} \quad \text{for} \quad i = 0, ...n-1$. This yields $2n$ equations:

$$P_i(x_i) = a_i = y_i \quad \text{for} \quad i = 0, ..., n-1 \tag{140}$$

and

$$P_i(x_{i+1}) = a_i + b_i h_i + c_i {h_i}^2 + d_i {h_i}^3 = y_{i+1} \quad \text{for} \quad i = 0, ..., n-1 \tag{141}$$

with $h_i = x_{i+1} - x_i$ being the distance between two adjacent points.
To be able to determine all the $4n$ coefficients, one needs to find $2n$ more restrictions on the polynomials.
Next, it is required that the first and second derivatives of two adjacent intervals match at the boundary of those intervals. This means that:

$$P_i^{'}(x_{i+1}) = P_{i+1}^{'}(x_{i+1}) \quad \text{and} \quad P_i^{''}(x_{i+1}) = P_{i+1}^{''}(x_{i+1}) \quad \text{for} \quad i = 0, ..., n-2 \tag{142}$$

These conditions yield another $n-1$ equations (there are n intervals, so there are $n-1$ intersection points between adjacent intervals):

$$b_{i+1} = b_i + 2c_i h_i + 3d_i {h_i}^2 \quad \text{for} \quad i = 0, ..., n-2 \tag{143}$$

and

$$2c_i + 6d_i h_i = 2c_{i+1} \quad \text{for} \quad i = 0, ..., n-2. \tag{144}$$

There are now $4n-2$ equations for these $4n$ unknowns. That means that two additional requirements for the polynomials are needed, in order to be able to fully solve the system of equations. One possibility is to set the second derivatives at the endpoints of the interval $[a, b]$ to 0, that is, $P_0^{''}(x_0) = 0$ and $P_{n-1}^{''}(x_n) = 0$.
By differentiating equation (139) twice for the two outermost intervals and plugging in x_0 and x_n respectively, this leads to the requirement that $c_0 = 0$ and $c_{n-1} = 0$.
A cubic spline with these additional requirements is called a natural cubic spline. This type of the cubic spline will also be used for the interpolation of the electronic structure factor S.
The next step is to solve these $4n-2$ equations to obtain the coefficients of the interpolating polynomial. Rearranging equation (144) for d_i and plugging it into

equation (141) yields an expression for b_i:

$$b_i = \frac{y_{i+1} - y_i}{h_i} - \frac{h_i}{3}(2c_i + c_{i+1}). \tag{145}$$

Plugging the newly found expressions for b_i and d_i into equation (143) yields equations exclusively for the c_i coefficients:

$$h_i c_i + 2(h_i + h_{i+1})c_{i+1} + h_{i+1}c_{i+2} = 3(\frac{y_{i+2} - y_{i+1}}{h_{i+1}} - \frac{y_{i+1} - y_i}{h_i}) \quad \text{for} \quad i = 0, ..., n-3. \tag{146}$$

This is now a system of n linear equations containing all the coefficients c_i for $i = 0, ..., n-1$. Since each equation only couples coefficients for three adjacent intervals, this is a tridiagonal system of equations for the c_i's. Special care needs to be taken for the first and last equations, i.e $i = 0$ and $i = n-3$, as they include coefficients whose values are already known. They look as follows:

$$h_0 \underbrace{c_0}_{=0} + 2(h_0 + h_1)c_1 + h_1 c_2 = 3(\frac{y_2 - y_1}{h_1} - \frac{y_1 - y_0}{h_0}), \tag{147}$$

and

$$h_{n-3}c_{n-3} + 2(h_{n-3} + h_{n-2})c_{n-2} + h_{n-2}\underbrace{c_{n-1}}_{=0} = 3(\frac{y_{n-1} - y_{n-2}}{h_{n-2}} - \frac{y_{n-2} - y_{n-3}}{h_{n-3}}). \tag{148}$$

As two of the n coefficients are already predetermined by requiring the spline to be natural, there remain only $n-2$ coefficients to be calculated. To better visualize this system of equations, one can write it down in the form $Ax = b$, where $A \in \mathbb{R}^{(n-2)\times(n-2)}$ and $x, b \in \mathbb{R}^{n-2}$. x contains the $n-2$ unknown coefficients $c_1, ..., c_{n-2}$ and b contains the values on the right side of equation (149) for $i = 1, ..., n-2$:

$$\begin{pmatrix} 2(h_0+h_1) & h_1 & & & & 0 \\ h_1 & 2(h_1+h_2) & h_2 & & & \\ & h_2 & 2(h_2+h_3) & h_3 & & \\ & & \ddots & \ddots & \ddots & \\ & & & h_{n-3} & 2(h_{n-3}+h_{n-2}) & \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ \\ c_{n-2} \end{pmatrix}$$

$$= 3 \begin{pmatrix} \frac{y_2-y_1}{h_1} - \frac{y_1-y_0}{h_0} \\ \frac{y_3-y_2}{h_2} - \frac{y_2-y_1}{h_1} \\ \vdots \\ \\ \frac{y_{n-1}-y_{n-2}}{h_{n-2}} - \frac{y_{n-2}-y_{n-3}}{h_{n-3}} \end{pmatrix} \quad (149)$$

There are several algorithms designed specifically to solve a tridiagonal linear system of equations. In this thesis, the Cholesky decomposition algorithm [12] will be used.

Consider a symmetric, positive definite matrix $A \in \mathbb{R}^{n\times n}$. The Cholesky decomposition algorithm finds a lower triangular matrix $L \in \mathbb{R}^{n\times n}$, such that $LL^T = A$ holds. One can think of this decomposition as a special case of the LR- decomposition, in which the upper triangular matrix R is the transpose of L.

The non diagonal entries of L can be calculated as follows:

$$L_{ij} = \frac{1}{L_{jj}} \left(A_{ij} - \sum_{k=1}^{j-1} L_{ik} L_{jk} \right) \quad for \quad i = j+1, j+2, ..., N. \quad (150)$$

The diagonal elements are given by:

$$L_{ii} = \sqrt{A_{ii} - \sum_{k=1}^{i-1} L_{ik}^2} \quad for \quad i = 1, 2, ..., N. \quad (151)$$

After succesfully applying the Cholesky decomposition, the system that remains to be solved is $LL^T x = b$ where L is a lower triangular matrix. This system can be solved by first substituting $L^T x = y$ and considering the system of equations $Ly = b$, which can be solved for the vector y by applying a forward substitution algorithm. Afterwards, the system $L^T x = y$ can be solved for x by a backwards substitution algorithm.

After solving the linear system of equations for the coefficients c shown in equation (149), equations (144) and (145) can be used to calculate the other $2n$ coefficients d and b. The coefficients a are already known by applying equation (140).

Once all $4n$ coefficients are known, the formula for the interpolating polynomial

$P(x)$ can be used to approximate arbitrarily many points within the interval $[a, b]$.

5.4 Calculation of ACFDT-RPA energies in VASP

VASP is a computer program designed for the quantum mechanical simulations of periodic systems such as crystals. To perform calculations, VASP needs a number of input files. Detailed information about the input files can be found in [15].
The `INCAR` file is the central input file. It determines, what kind of calculations VASP performs and how to perform them. A wide variety of parameters can be specified here.
The `KPOINTS` file determines the number and positions of the k-points in the Brillouin zone.
The `POTCAR` file contains the pseudopotentials and the frozen core electrons for the atomic species which are used for the the specific caculations. The frozen core approximation assumes that only valence electrons are contributing to the interaction between atoms. The effect of electrons close to the nucleus will be ignored. In addition, the projector augmented wave method (PAW) is used [16] [17]. The PAW method provides a tool to transform the rapidly oscillating wavefunctions of valence electrons into smoother pseudo wavefunctions. For materials containing more than one species of atoms, the different `POTCAR` files have to be concatenated into one file.
The `POSCAR` file holds all the information about the lattice and basis of the system. The first entry consists of the three lattice vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ defining the Bravais lattice. They are scaled by the lattice constant a, which can be supplied individually. In the next line, the numbers and species of the atoms in the basis of the structure are entered. The atomic positions can then be entered in Cartesian or in direct coordinates. Direct coordinates means that the three lattice vectors are used as a basis to describe the positions of the atoms in the unit cell. The position vector of an atom is then given by $\vec{x} = \sum_{i=1,3} x_i \vec{a}_i$. In Cartesian coordinates, the position vector is scaled by the lattice constant:

$$\vec{x} = a \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}. \tag{152}$$

The energy of the ACFDT-RPA groundstate E^{RPA} is the sum of the ACFDT RPA correlation energy E_c, which is calculated using equation (137) and the Hartree-Fock energy E_{HF}.
In the current edition of VASP, the calculation of the RPA correlation energy is implemented in four separate steps. In each of these steps, the `INCAR` file needs to be modified in order to control the tasks that VASP performs. The `POSCAR` and

KPOINTS file remains unmodified. What follows, is a description of these steps. They can be found in more detail in [15] and [18]:
The first step is a DFT calculation. The occupied orbitals satisfying the Kohn Sham equation (27) are calculated. Gaussian smearing with a width of 0.05eV is used for the partial occupancies. The corresponding tags in the INCAR file are ISMEAR=0 and SIGMA=0.05. These two tags are used throughout all four steps but will only be mentioned here.
In addition, EDIFF=1E-8 is set. The EDIFF tag specifies the global break condition for the electronic self consistency loops. That means that the self consistency loop stops if the change in the energy eigenvalues and the total energy between two consecutive steps is smaller than the value specified in EDIFF. In preparation for the third step, the OUTCAR file of this VASP run will be saved.
In the second step, the Hartree-Fock energy is calculated using the DFT orbitals from the first step. To do this, the tag LHFCALC=.TRUE. is set. It specifies that Hartree-Fock/DFT hybrid functional type calculations should be performed. The NELM tag, which sets the maximum number of electronic self consistency steps, is being set to 1, since the convergence of the DFT orbitals has already been performed in step 1.
The AEXX tag specifies the amount of the exact exchange energy with the amount of LDA exchange being 1-AEXX. It is being set to AEXX=1, which means that there is no LDA exchange energy.
In addition, the tag ALGO=Eigenval allows to recalculate one electron energies and perform selected postprocessing using the current electron orbitals stored in the WAVECAR file. To prevent VASP from writing the wavefunctions of the current run into the WAVECAR file and therefore overwriting the orbitals from step 1, LWAVE=.FALSE. is set. The OUTCAR file of this VASP run needs to be stored, since it contains the Hartree-Fock energy that is needed to calculate the ACFDT-RPA groundstate energy.
In the third step, the tag ALGO=Exact is set which tells VASP to perform an exact diagonalization of the DFT Hamiltonian. Now, the OUTCAR file from the first run has to be searched for the string "maximum number of plane-waves". This value is rounded up to the next higher number that is a multiple of the number of cores used for the calculation. Afterwards, the tag NBANDS will be set to this value in the INCAR file. For example, if the calculation is performed on 8 cores and the "maximum number of plane waves" is 500, then NBANDS will be set to 504, since 504 is the smallest number greater than 500 and divisible by 8. The tag NELM=1 is set due to the same reasons as in step 2. Additionally, LOPTICS=.FALSE. is set to avoid calculating the frequency dependent dielectric matrix and head contributions to the correlation energy. These head contributions will be discussed later.

In the fourth and final step, the ACFDT-RPA correlation energy is calculated. This is done by setting the tag `ALGO=ACFDT`. The ACFDT-RPA correlation energy is given by:

$$E_c = \frac{1}{2\pi} \int d\omega \sum_{\vec{q}\in BZ} \sum_{\vec{G}} \left(\left(\ln\left(1 - \chi^{KS}(\vec{q}, i\omega) v(\vec{q})\right) \right)_{\vec{G},\vec{G}} + v_{\vec{G},\vec{G}}(\vec{q}) \chi^{KS}(\vec{q}, i\omega) \right). \quad (153)$$

The number of sampling points for the ω integration in E_c is given by the `NOMEGA` tag. In this thesis, `NOMEGA=8` was set [2]. In RPA calculations, the computation and storage of the response function $\chi^0_{\vec{q}}(\vec{G}, \vec{G}', \omega)$ dominates the computational cost. The number of $\vec{G}$-vectors included in the response function is therefore truncated at a certain vector $\vec{G}_{cutoff}$ which is determined by the `ENCUTGW` tag. All vectors, which yield a smaller energy than the cutoff energy E^{GW}_{cut} are included in the calculation, i.e all vectors $\vec{G}$ that satsify:

$$\frac{\hbar^2 \mid \vec{q} + \vec{G} \mid^2}{2m_e} < E^{GW}_{cut} = \frac{\hbar^2 \mid \vec{G}_{cutoff} \mid^2}{2m_e}. \quad (154)$$

VASP then automatically extrapolates the correlation energy to an infinite number of $\vec{G}$-vectors using a linear regression of the form:

$$E_c(N_{\vec{G}}) - E_c(\infty) = \frac{A}{N_{\vec{G}}}, \quad (155)$$

where $N_{\vec{G}}$ is the number of $\vec{G}$ vectors that are included in the calculation. The converged value of this regression can be found in the `OUTCAR` file of this run (search for the line that starts with "converged value"). After following this procedure, one knows both the Hartree-Fock energy and the ACFDT-RPA correlation energy. Adding up these two values results in the ACFDT-RPA groundstate energy per unit cell of the desired system.

5.5 Extraction of the electronic structure factor

A necessary preliminary for the interpolation of the structure factor is the explicit calculation of the electronic structure factor $S(\vec{q} + \vec{G}, \vec{q} + \vec{G}')$ as this has not been performed yet in VASP. The goal is to create a three dimensional array, called `STUFAK`, in which the values of the structure factor will be stored. To accomplish this, first the size of this array has to be determined. This can be achieved by considering the cutoff energy E^{GW}_{cut} for the plane wave basis set in order to find a physical interpretation of the length of a wave vector $\left|\vec{q} + \vec{G}\right|$. The energy of a plane wave with wave vector $\vec{q} + \vec{G}$ is proportional to the square of the length of the wave vector $\left|\vec{q} + \vec{G}\right|^2$. Therefore, the squareroot of the energy cutoff $\sqrt{E^{GW}_{cut}}$

will be proportional to the length of the wave vector $\left|\vec{q}+\vec{G}\right|$ and can be interpreted physically as the maximum length that a wave vector is allowed to have in order to be included in the calculation of the response function.
Each wave vector corresponds to a point in reciprocal space. In order to find how many wave vectors will be included in each spatial direction of reciprocal space, one therefore needs to divide the squareroot of the energy cutoff $\sqrt{E_{cut}^{GW}}$ by the length of the reciprocal basis vector in the corresponding direction. As this is only supposed to give a schematic overview over the coding process, the fact that the energy and the reciprocal basis vectors need to be converted to matching unit systems, will be ignored. Additionally, this number has to be multiplied with the number of k-points in the corresponding direction $N_{KPTS,i}$ as they determine the refinement of the reciprocal lattice in each spatial direction.

$$N_i = \frac{\sqrt{E_{cut}^{GW}}}{\mid \vec{b}_i \mid} N_{KPTS,i} \quad for \quad i = 1,2,3 \tag{156}$$

Each wave vector has an equivalent wave vector pointing in the opposite direction yielding the same energy. Therefore, the number of points in reciprocal space in each direction that are included in the calculation will be $2N_i + 1 \quad for \quad i = 1,2,3$. The array `STUFAK` is therefore allocated with sizes $-N_1 : N_1$, $-N_2 : N_2$, $-N_3 : N_3$. This ensures that all values of the structure factor can be stored in the array `STUFAK`.
For the calculation of the RPA correlation energy, only the diagonal elements of the structure factor $S(\vec{q}+\vec{G}, \vec{q}+\vec{G}) \equiv \overline{S}(\vec{q}+\vec{G})$ are needed, as can be seen in equation (137). For each wave vector $\vec{q}+\vec{G}$ which is included in the calculation by VASP, only this diagonal element $\overline{S}(\vec{q}+\vec{G})$ will be stored in the array `STUFAK`.
Each element of the array `STUFAK` is therefore uniquely identified by three values: Either the three indices to navigate through `STUFAK`, $\{i,j,k\}$, or the three components of the vector $\vec{q}+\vec{G}$ have to be provided. There exists a one to one correspondence between these two sets of three numbers, which is given by the following equation:

$$\begin{pmatrix} \left(\vec{q}+\vec{G}\right)_1 \\ \left(\vec{q}+\vec{G}\right)_2 \\ \left(\vec{q}+\vec{G}\right)_3 \end{pmatrix} = \begin{pmatrix} \frac{b_{1,1}}{N_{KPTS,1}} & \frac{b_{2,1}}{N_{KPTS,1}} & \frac{b_{3,1}}{N_{KPTS,1}} \\ \frac{b_{1,2}}{N_{KPTS,2}} & \frac{b_{2,2}}{N_{KPTS,2}} & \frac{b_{3,2}}{N_{KPTS,2}} \\ \frac{b_{1,3}}{N_{KPTS,3}} & \frac{b_{2,3}}{N_{KPTS,3}} & \frac{b_{3,3}}{N_{KPTS,3}} \end{pmatrix} \begin{pmatrix} i \\ j \\ k \end{pmatrix} = A \begin{pmatrix} i \\ j \\ k \end{pmatrix}. \tag{157}$$

$b_{i,j}$ denotes the j-th component of the i-th reciprocal basis vector.
Next, the procedure of filling the values of the structure factor into the array `STUFAK` will be discussed.
VASP first determines the number of $\vec{q}$ vectors in the first Brillouin zone which will be included in the calculation. This number depends both on the k-point mesh

entered in the KPOINTS file and whether or not symmetry procedures are used. If symmetry is switched on, only $\vec{q}$ vectors from the irreducible Brillouin zone (IBZ) will be used for calculating contributions to the correlation energy. All other $\vec{q}$ vectors not lying in the IBZ would only yield identical contributions. Omitting these calculations and only multiplying the results of $\vec{q}$ vectors from the IBZ by an appropriate weighting factor saves computation time.

An outer loop is then performed running over the set of all $\vec{q}$ vectors. Each of these vectors is passed to the subroutine XI_ACFDT_ALL_RPA successively. The array STUFAK is defined as a global variable and is allocated with the appropriate size during the first call to this subroutine. Within this subroutine, all $\vec{G}$ vectors, fulfilling the condition for the energy cutoff in equation (154), are generated. Each separate call to the XI_ACFDT_ALL_RPA subroutine has therefore only access to the set of $\vec{q}+\vec{G}$ vectors for one specific $\vec{q}$ vector, which will be a subset of all possible $\vec{q}+\vec{G}$ vectors for this system. A call to a separate subroutine SQ_EXTRACT calculates the value of the structure factor $\overline{S}(\vec{q}+\vec{G})$ for this subset of $\vec{q}+\vec{G}$ vectors while simultaneously performing the ω - integration in equation (136). SQ_EXTRACT then uses the one to one correspondence in equation (157) to determine the location of $\overline{S}(\vec{q}+\vec{G})$ within STUFAK for each $\vec{G}$ vector. This is done by applying the inverse matrix A^{-1} to every unique $\vec{q}+\vec{G}$ vector, yielding the indices $\{i,j,k\}$ and then storing the value $\overline{S}(\vec{q}+\vec{G})$ in STUFAK(i,j,k).

At the end of one call to XI_ACFDT_ALL_RPA, the values of the structure factor $\overline{S}(\vec{q}+\vec{G})$ have been calculated and stored in STUFAK only for the $\vec{q}+\vec{G}$ vectors that were passed to the routine. Therefore, STUFAK is gradually filled during each call to the subroutine XI_ACFDT_ALL_RPA. After the last call, all combinations of $\vec{q}+\vec{G}$ vectors and the corresponding values of S are stored in STUFAK.

The array POTFAK_SQ is used to store the values of the Fourier transformed Coulomb potential for all $\vec{q}+\vec{G}$ vectors. Its value is given by $\frac{4\pi}{|\vec{q}+\vec{G}|^2}$. It is gradually filled in an identical way to STUFAK.

When the values for all possible combinations of $\vec{q}+\vec{G}$ vectors for the specific system are stored in the arrays STUFAK and POTFAK_SQ, equation (137) can be used to calculate the correlation energy. This implementation provides an alternative to using equation (126), where it isn't necessary to explicitely calculate the structure factor.

The reason for this additional work will become apparent in the next section when the tricubic spline interpolation will be discussed.

5.6 Tricubic Spline Interpolation of the electronic structure factor

Calculating the RPA correlation energy for a fine k-point mesh consumes a lot of computation time compared to a DFT calculation. That is the reason why it is beneficial to come up with a method to accelerate these calculations. Inspired by [19], the approach presented here consists of calculating the electronic structure factor exactly for a relatively coarse k-point mesh and then using tricubic spline interpolation to approximate the values of the structure factor for a finer k-point mesh. The tricubic spline interpolation is computationally less expensive than the exact calculation of the strcuture factor, however, it comes with the obvious disadvantage that the interpolated values will differ from the real values by some margin. To keep this margin as small as possible, it is necessary to carefully choose the interpolation algorithm. In the following, the interpolation procedure, as it has been implemented during this Master's thesis, will be discussed in detail.

Both the structure factor and the Coulomb potential are known at all values of $\vec{q}+\vec{G}$ vectors for the chosen initial k-point mesh. These values are stored in the arrays `STUFAK` and `POTFAK_SQ` respectively. The desired outcome of the tricubic spline interpolation of the structure factor is a bigger array `INTSTUFAK` containing both the originally known values from `STUFAK`, as well as the interpolated values. Interpolating between the values of the Coulomb potential in `POTFAK_SQ` is not necessary, since it is an analytically known function that can be evaluated at arbitrarily many points in reciprocal space.
First, the dimensions of the new array have to be determined. A set of three natural numbers $\{n_1, n_2, n_3\}$ specifies the refinement of `STUFAK` in the spatial dimensions. If `STUFAK` contains $2N_i + 1$ values in the i-th spatial dimension, then `INTSTUFAK` will require storage space for $2n_iN_i + 1$ values in the i-th spatial dimension. This choice guarantees that each exact value of the structure factor in `STUFAK` will also be stored in `INTSTUFAK`.
The tricubic spline interpolation of `STUFAK` will be performed by a single call to a subroutine `TRICUBIC_INTERPOLATION`. Before calling this subroutine, `INTSTUFAK` is allocated and initialized to 0. Then, after the array `STUFAK` has been filles with all the values of the structure factor, both `STUFAK` and `INTSTUFAK` will be passed to `TRICUBIC_INTERPOLATION`, where the spline interpolation will be performed subsequently in each of the three spatial dimensions. The functioning of this subroutine will be explained in the following:
At first, a cubic spline interpolation will be performed on the first spatial dimension of `STUFAK`. An outer loop runs over all combinations of pairs of the second and third

index of STUFAK. Therefore, for each cycle, 2 spatial dimensions are kept fixed which leaves a unique vector of $2N_1 + 1$ values, namely STUFAK(:,j,k). The algorithm for the cubic spline interpolation is then performed on the identified vector. In accordance with the notation used before, the x_i values correspond to the indices

$$-N_1, -N_1 + 1, ..., N_1 - 1, N_1 \tag{158}$$

of STUFAK, while the y_i values correspond to the values of STUFAK at the specified indices:

$$\texttt{STUFAK}(-\texttt{N}_1, \texttt{j}, \texttt{k}), \texttt{STUFAK}(-\texttt{N}_1 + 1, \texttt{j}, \texttt{k}), ..., \texttt{STUFAK}(\texttt{N}_1 - 1, \texttt{j}, \texttt{k}), \texttt{STUFAK}(\texttt{N}_1, \texttt{j}, \texttt{k}). \tag{159}$$

The number n_1 determines the number of intermediary points for which the interpolation polynomial will be evaluated. The results yield the approximated values for the structure factor at the desired points. They will be stored in the array INTSTUFAK, whose size is chosen in accordance with the multiplying factor n_1. In the following figures, the interpolation process will be demonstrated with the help of a two dimensional array:

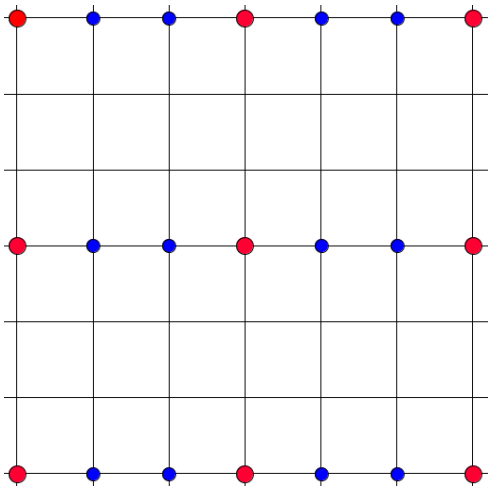
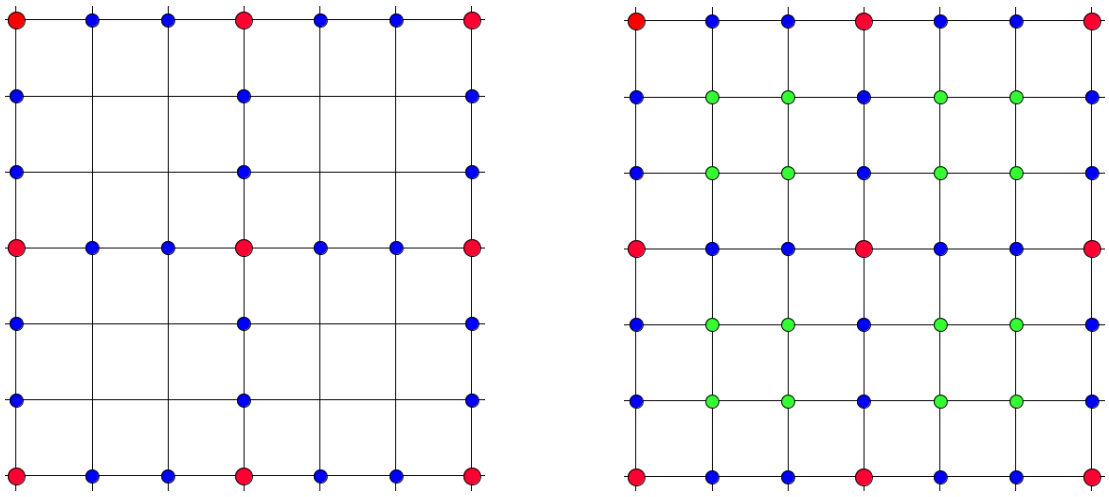


Figure 1: The figure above displays two different grids. The coarser grid, defined by the red dots, displays the array STUFAK. Each red dot denotes an explicitely calculated value of the structure factor. The finer grid corresponds to the array INTSTUFAK. For each fixed value of the second spatial dimension of STUFAK, a cubic spline interpolation is performed along the first spatial dimension. The resulting interpolated values of the structure factor are depicted as blue dots.

The interpolation procedure will then be performed for the other two dimensions as well. It is important to note that after the first outer loop is finshed, all of the originally known values of the structure factor (red dots), as well as the refinement along the first spatial dimension (blue dots) are stored in the array INTSTUFAK.
The interpolation along the second spatial dimension is performed, by keeping each

value of the first spatial dimension of `INTSTUFAK` fixed. This ensures that information about the structure factor at the interior points (green dots in figure (2b)) is not lost.



(a) (b)

Figure 2: Performing an interpolation along the second spatial dimension for each fixed value of the first spatial dimension of STUFAK leads to figure (2a). Note that some interior points of INTSTUFAK are missing using this method. Information about the structure factor at these missing points, denoted by green dots in figure (2b), can only be recovered by performing an interpolation for all fixed values of the first spatial dimension of INTSTUFAK.

As was mentioned before, each entry of STUFAK and INTSTUFAK uniquely corresponds to a $\vec{q}+\vec{G}$ vector. Therefore, after applying tricubic interpolation on the array STUFAK, the summation in equation (137) can be replaced by

$$E_c = \sum_{\{i,j,k\}} INTSTUFAK(i,j,k) \cdot INTPOTFAK\_SQ(i,j,k). \tag{160}$$

This summation will range over a far bigger set of vectors. The more detailed the structure factor is known, the better the approximation to the RPA correlation energy will be. In the next section, the results of the interpolation and their effects on the correlation energy will be presented for different materials.

6 Results

In this section, the interpolation of the structure factor will be tested for different materials. It will be investigated whether the interpolation yields reliable results for the correlation energy and if it saves computational time without introducing too much noise. In the following, we present a figure for each of the materials which were chosen to test the interpolation: cubic diamond, boron nitride (cubic and hexagonal), cubic silicium and gallium arsenide. In addition, the interpolation was also tested for a system, where water is adsorpted on boron nitride. All of the plots include three different methods to calculate the RPA correlation energy.
The first set of calculations will be performed with the standard edition of VASP, which makes use of equation (126) to calculate the RPA correlation energy.
This method yields the same result as storing the values of the structure factor in the array `STUFAK` first and then applying equation (137) to calculate the correlation energy. This is due to the fact that equation (137) is just a reformulation of equation (126). However, for later purposes, using formula (137) has the advantage that an interpolation can be performed on the array `STUFAK` yielding the array `INTSTUFAK`.
The second method consists of performing a tricubic spline interpoaltion on the structure factor and then using equation (160) with the refined arrays `INTSTUFAK` and `INTPOTFAK_SQ`. It will be shown that this method leads to a faster convergence of the RPA correlation energy with respect to the number of k-points.
The third set of calculations will be performed by including head contributions in the calculation of the correlation energy. To understand what head contributions to the correlation energy are, picture again how the correlation energy is calculated in the modified version of VASP:

$$E_c = Tr(vS) = \sum_{\vec{q}+\vec{G}} v(\vec{q}+\vec{G})S(\vec{q}+\vec{G}). \tag{161}$$

The structure factor S and the Fourier transformed Coulomb potential v are actually matrices, depending on the two vectors $\vec{q}+\vec{G}$ and $\vec{q}+\vec{G}'$, i.e $S(\vec{q}+\vec{G},\vec{q}+\vec{G}')$ and $v(\vec{q}+\vec{G},\vec{q}+\vec{G}')$. However, for the calculation of the correlation energy E_c, only the diagonal elements of S and v, where $\vec{G}=\vec{G}'$ are needed.
An important point to consider is the contribution to the correlation energy in (161), if $\vec{q}+\vec{G}$ approaches $\vec{0}$. The Fourier transformed Coulomb potential is proportional to $\frac{1}{\left|\vec{q}+\vec{G}\right|^2}$, while the elctronic structure factor is proportional to $|\vec{q}|^2$ in the limit $q \to 0$. Taking the product cancels these two dependencies and a numerical value remains which is added to the correlation energy. This contribution is called the head contribution to E_c as it contains the information of S stored in the first column entry of the first line of the matrix $S(\vec{q}+\vec{G},\vec{q}+\vec{G}')$. The `LOPTICS` tag controls, whether

VASP includes this contribution or not.
In the modified version of VASP, the tag `LOPTICS=.FALSE.` is set, which manually sets the diverging Coulomb kernel to 0 for $\vec{q} + \vec{G} \to \vec{0}$. As a result, the product $S(\vec{0})v(\vec{0})$ is 0 and head contributions to the correlation energy E_c are ignored. However, the idea is that after tricubic spline interpolation of the structure factor close to $\vec{0}$, the head contribution to E_c won't be of significance anymore, since there are a sufficient number of points close to $\vec{0}$, which all give a nonzero contribution to the correlation energy. The finer the interpolation grid, the less important the head contribution is.
In the standard version of VASP, the `LOPTICS` tag is usually set to `.TRUE.`, therefore including head contributions to E_c. Additionally, in combination with `LOPTICS=.TRUE.` the tag `LPEAD=.TRUE.` can be set, which tells VASP to calculate the derivative of the cell periodic parts of the orbitals with respect to $\vec{q}$ by using finite differences. Increasing the number of k-points with additionally including the head contribution should have a similar effect as a tricubic spline interpolation of the structure factor S without any head contributions.
Therefore, the third set of calculations will be performed with the tag `LOPTICS=.TRUE.` set in the standard version of VASP.
The following plots display the relation between the RPA correlation energy of various materials and the inverse number of k-points $\frac{1}{N_k}$.
The purple crosses throughout the next figures are showing correlation energies calculated with the standard version of VASP for a specific k-point grid.
The blue crosses are obtained by using equation (160) with the interpolated array `INTSTUFAK`. Additionally, a refinement of `POTFAK_SQ` is calculated as well by simply plugging the new $\vec{q}+\vec{G}$ vectors into the formula for the Fourier transformed Coulomb potential. It is these crosses that are of main interest, since they are expected to converge much faster to the true value of the RPA correlation energy.
The red crosses display correlation energies with head contributions included.
In addition, an extrapolation of the correlation energy without head contributions to $\frac{1}{N_k} = 0$ is performed. This will yield an estimate for the correlation energy for an infintely fine k-point grid.

6.1 Isolators

The following three figures display the three different methods to calculate the RPA correlation energy for cubic diamond, cubic boron nitride and hexagonal boron nitride.

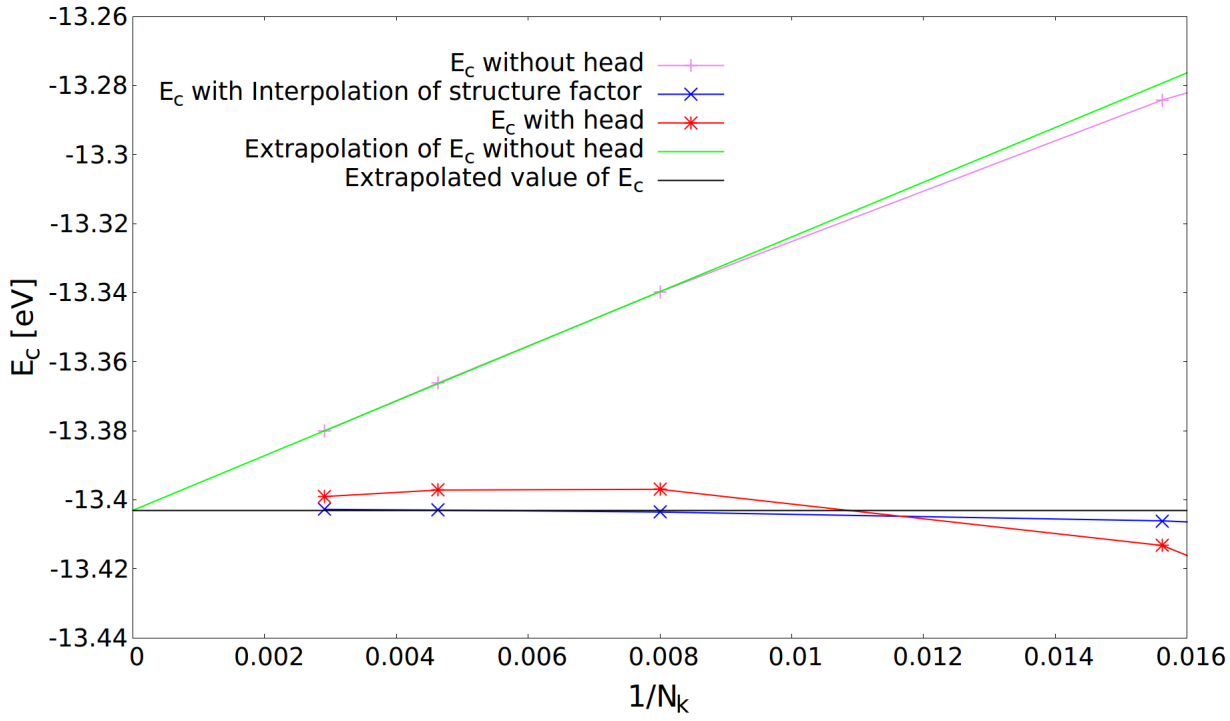


Figure 3: The figure depicts the convergence of the RPA correlation energy with an increasing number of k-points for cubic diamond. The fastest convergence of E_c is obtained by interpolation of the structure factor.

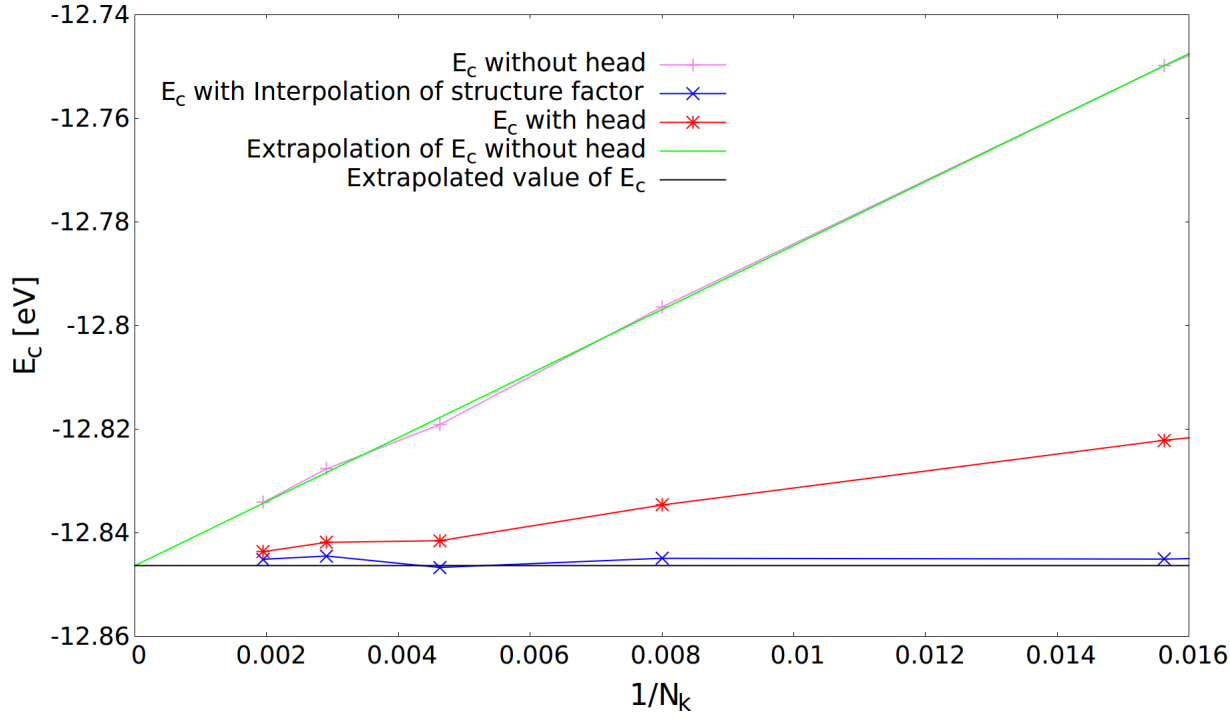


Figure 4: The figure depicts the convergence of the RPA correlation energy with an increasing number of k-points for cubic boron nitride. The fastest convergence of E_c is obtained by interpolation of the structure factor.

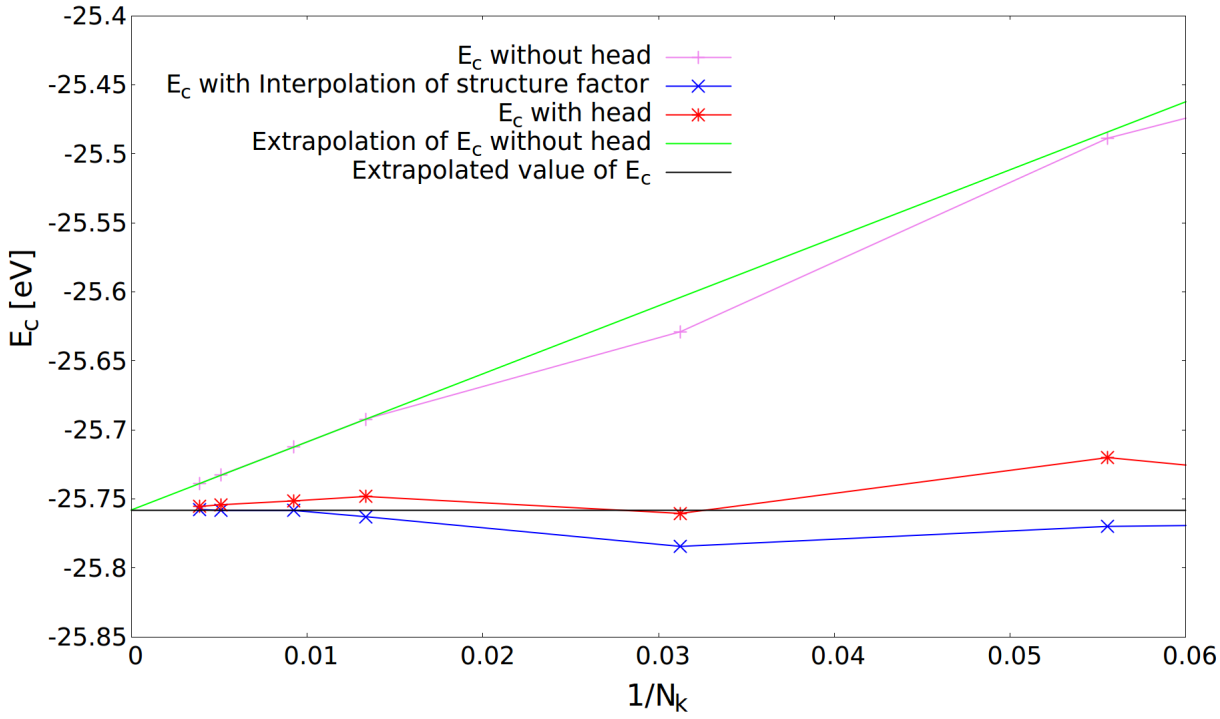


Figure 5: The figure depicts the convergence of the RPA correlation energy with an increasing number of k-points for hexagonal boron nitride. The fastest convergence of E_c is obtained both by interpolation of the structure factor and by including head contributions.

The values of the correlation energy obtained by interpolation of the structure factor converge faster than the values obtained by the other methods. In this context, convergence of the correlation energy has been achieved, once there is no more significant change in E_c for a finer k-point mesh. For cubic diamond and cubic boron nitride, convergence of the correlation energy is reached for a k-point mesh of 4×4×4, if the interpolated structure factor is used to calculate E_c. However, when using the original VASP code with or without head contributions to calculate E_c, convergence has not been reached for the same choice of a k-point mesh. A difference of approximately 1% between 8×8×8 and 4×4×4 k-points can be observed, when comparing the non-interpolated values of E_c.

Thus, interpolating the structure factor has the same effect as using a finer k-point mesh at which formula (126) is then evaluated exactly. In addition, the interpolation provides the advantage that it consumes far less computational time than explicitly evaluating equation (126) for the finer grid. This is due to the effort needed to calculate the exact value of the structure factor at an additional $\vec{q}+\vec{G}$ vector. First, the linear response function needs to be computed and stored. Second, the ω integration in equation (126) needs to be performed. Finally, the Trace of $ln(1-\chi^{KS}v)+\chi^{KS}v$ needs to be calculated.

In a tricubic spline interpolation, the most demanding task is to solve linear systems

of equations and evaluate the interpolation polynomials afterwards. This is computationally less costly.
Similar conclusions for hexagonal boron nitride can be drawn from figure (5).
It can be seen that for cubic diamond and cubic boron nitride, the fastest convergence of the RPA correlation energy is observed for tricubic interpolation of the structure factor. Additionally, as expected, including head contributions has a similar effect as the interpolation. While the values obtained by interpolation have nearly converged for a relatively coarse k-point mesh, the values obtained by including head contributions are still fluctuating around this converged value. For a higher number of k-points, e.g `4×4×4` k-points in figure (3) or `6×6×3` k-points in figure (5), the two methods yield approximately the same result. This suggests that tricubic spline interpolation of `STUFAK` does replace the need to include head contributions in equation (137), since the refined grid will provide sufficient information about the structure factor close to $\vec{0}$.
The region around $\vec{0}$ is, where the interpolation is needed the most. The exact structure factor varies a lot in this region, which increases the need for an accurate interpolation in order to aproximate the correlation energy. For larger $\vec{q}+\vec{G}$ vectors however, the structure factor is a smooth function, making a detailed interpolation less important in that region.
For hexagonal boron nitride, interpolation of `STUFAK` has approximately the same effect as including head contributions.

6.2 Semiconductors

In this section, the three different methods to calculate the RPA correlation energy are performed for two semiconducting materials, silicon and gallium arsenide. The results are displayed in the following two figures.

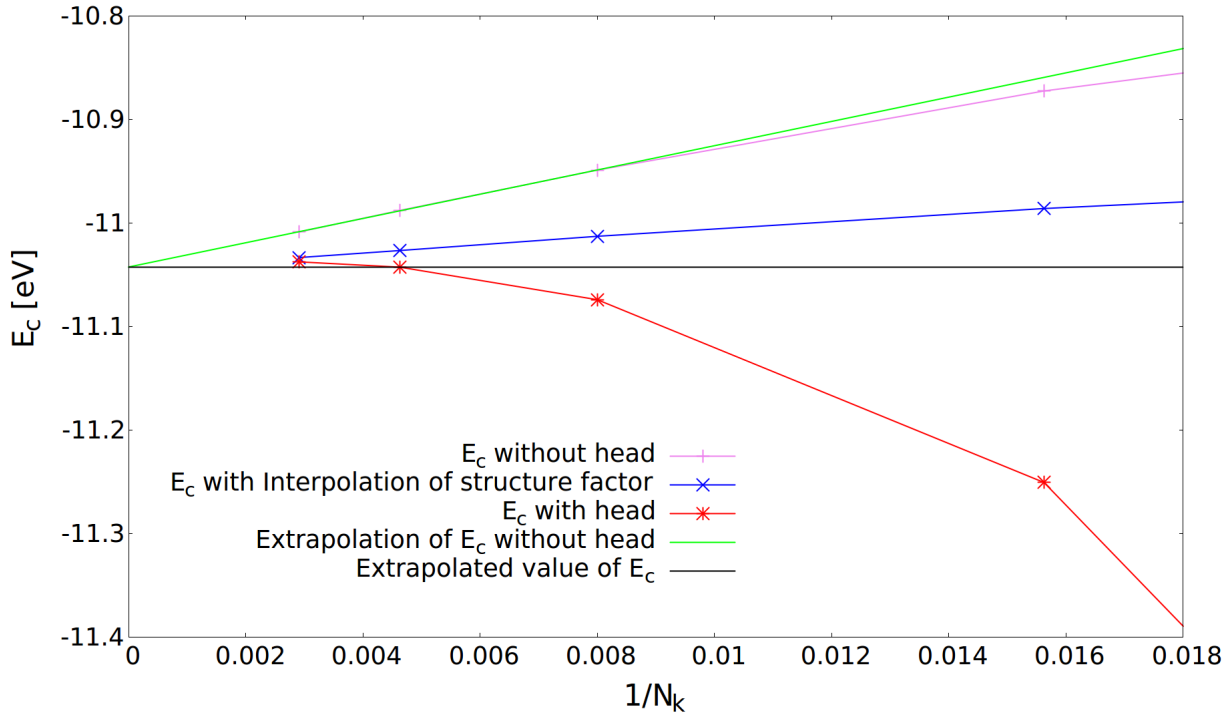


Figure 6: The figure depicts the convergence of the RPA correlation energy with an increasing number of k-points for cubic gallium arsenide. The fastest convergence of E_c is obtained by interpolation of the structure factor.

The correlation energy of the semiconducting material gallium arsenide displays a similar behavior as the three insulators. As can be seen in figure (6), the interpolation of the structure factor yields the fastest convergence. Additionally, including head contributions only improves the convergence if a k-point mesh of $6 \times 6 \times 6$ or finer is chosen.

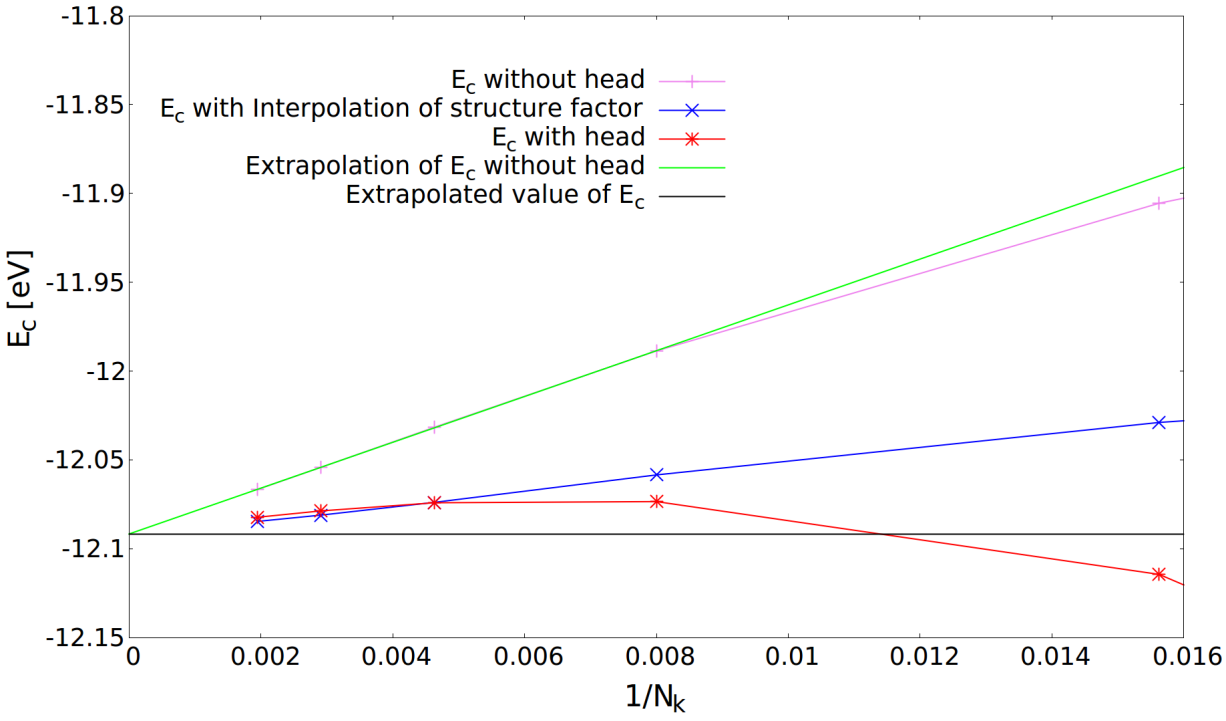


Figure 7: The figure depicts the convergence of the RPA correlation energy with an increasing number of k-points for cubic silicon. The fastest convergence of E_c is obtained by interpolation of the structure factor.

For silicon, both the interpolation of the structure factor, as well as the inclusion of head contributions leads to an increased convergence of the RPA correlation energy. However, there is no significant difference between these two methods for silicon.
Although the interpolation significantly improves the convergence of the RPA correlation energy for insulators, it does not work as well for semiconductors. For insulators, convergence of the interpolated correlation energy already occurs for coarse k-point meshes such as $3 \times 3 \times 3$ for cubic diamond. This is not the case for semiconductors, where convergence is achieved only for finer k-point meshes. A possible explanation for this behavior could lie in the different sizes of the band gaps for the two classes of materials.
To understand this, one property of equation (79) needs to be investigated. The denominator contains the energy difference between two bands at different reciprocal vectors $\frac{1}{\epsilon_{m\vec{k}'} - \epsilon_{n\vec{k}}}$. For semiconductors, the band gap between valence band and conduction bands is small compared to insulators, therefore, these contributions to the response function will be very large. The sampling of reciprocal space needs to be chosen in such a way that the largest contributions are taken into account. As a result, a fine k-point mesh is necessary to reach a converging correlation energy. For silicon, the situation is especially delicate, since it has an indirect band gap. Its band structure is depicted in figure (10).

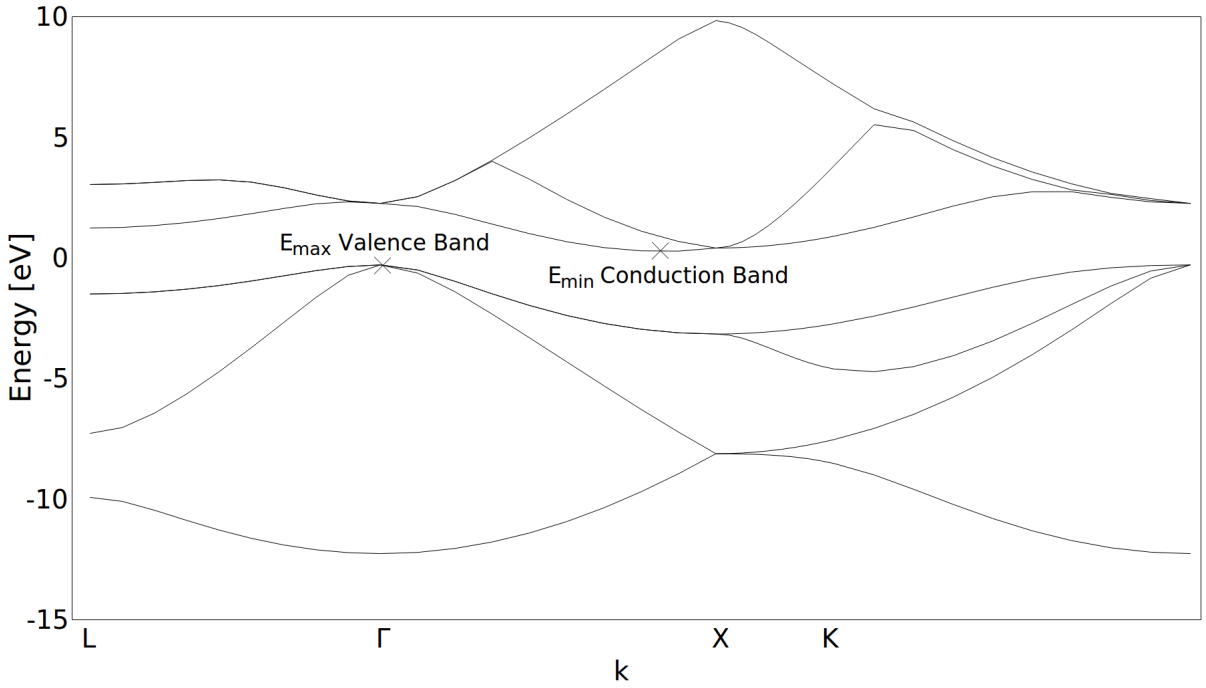


Figure 8: The figure depicts the band structure of silicon as calculated by VASP. The experimentally measured band gap of silicon is 1.11 eV at 300 Kelvin [20]. This makes it the smallest band gap of all the tested materials.

A band gap is called an indirect band gap, if the minimal energy in the conduction band occurs at a different k-vector than the maximal energy in the valence band. This is shown in figure (10). The sampling needs to be refined, such that the Brillouin zone is sampled sufficiently close to both these k-vectors. Otherwise, the largest contribution to the response function will be missing and an inaccurate result for the correlation energy is obtained.
For insulators, the band gap is bigger. Therefore the contributions in equation (79) will vary less over the Brillouin zone. It is thus not necessary to refine the k-point mesh to such a degree in order to achieve convergence.

6.3 Adsorption of water on boron nitride

As a final test for the interpolation, the adsorption of water on a boron nitride surface is investigated. In an adsorption process, an external material, called adsorbate, is placed on a surface, called adsorbent. The adsorption energy per unit cell of this system is defined as follows:

$$E_{ads} = E(\mathrm{H_2O} \cup \mathrm{BN}) - E(\mathrm{H_2O}) - E(\mathrm{BN}), \tag{162}$$

where $E(\mathrm{H_2O})$ and $E(\mathrm{BN})$ are the energy per unit cell of water and boron nitride respectively. $E(\mathrm{H_2O} \cup \mathrm{BN})$ is the energy per unit cell of the combined system.

Previous reserch has shown that semilocal density functionals tend to underestimate the adsorption energy [21]. However, applying the RPA to surfaces and adsorption processes yields better results for both lattice constants as well as adsorption energies [22]. The calculation of the adsorption energy is performed in three seperate steps. First, the ACFDT-RPA groundstate energy per unit cell of water, the adsorbate, is calculated. This is done by performing the same four subsequent calculations as for insulators and semiconductors. The following figure shows a visualization of the structure using p4vasp.

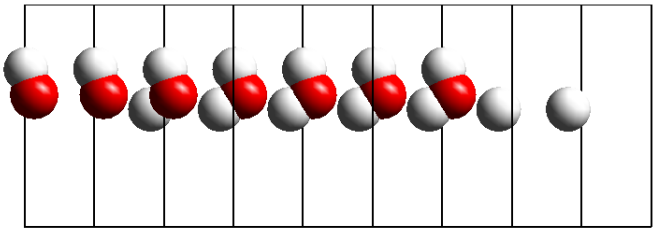


Figure 9: The figure depicts a supercell with multiple water molecules. The red spheres represent oxygon atoms while the white spheres represent hydrogen atoms. The calculations were performed with cells including only one water molecule.

The same calculations are performed for boron nitride, the adsorbent. The following figure shows a visualization of the structure using p4vasp.

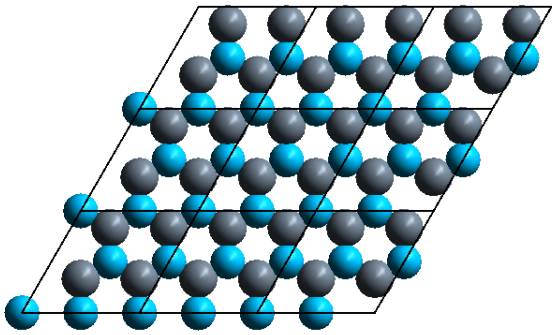
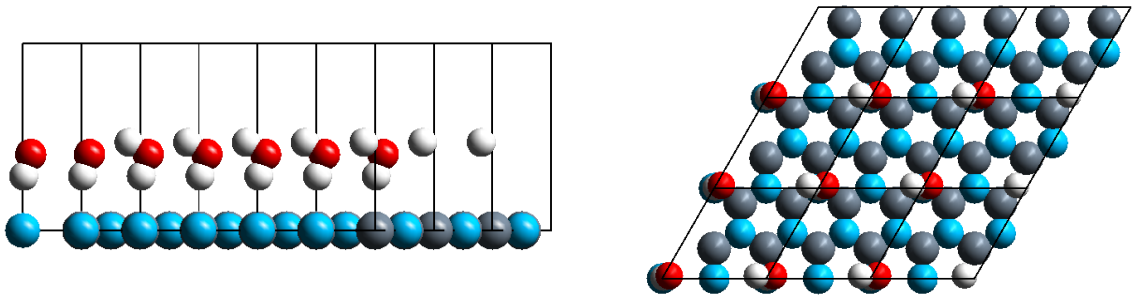


Figure 10: The figure depicts a boron nitride supercell. The blue spheres depict nitrogen atoms while the grey spheres represent boron atoms. The calculations were performed with smaller cells including only a single boron nitride unit cell.

In the final step, the ACFDT-RPA groundstate energy per unit cell of the combined system, adsorbate and adsorbent, is calculated. The following figure shows a visualization of the structure using p4vasp.



(a) (b)

Figure 11: The figure depicts the combined system of boron nitride and water on top of it. The structure is shown from the side view and the top view.

In equation (162), E_{ads} includes both the Hartree-Fock energy as well as the ACFDT-RPA correlation energy. To investigate the performance of the tricubic spline interpolation, only the ACFDT-RPA correlation energy part of the adsorption energy will be taken into account:

$$E_c^{ads} = E_c(\mathrm{H_2O} \cup \mathrm{BN}) - E_c(\mathrm{H_2O}) - E_c(\mathrm{BN}). \tag{163}$$

The results are displayed in the following figure.

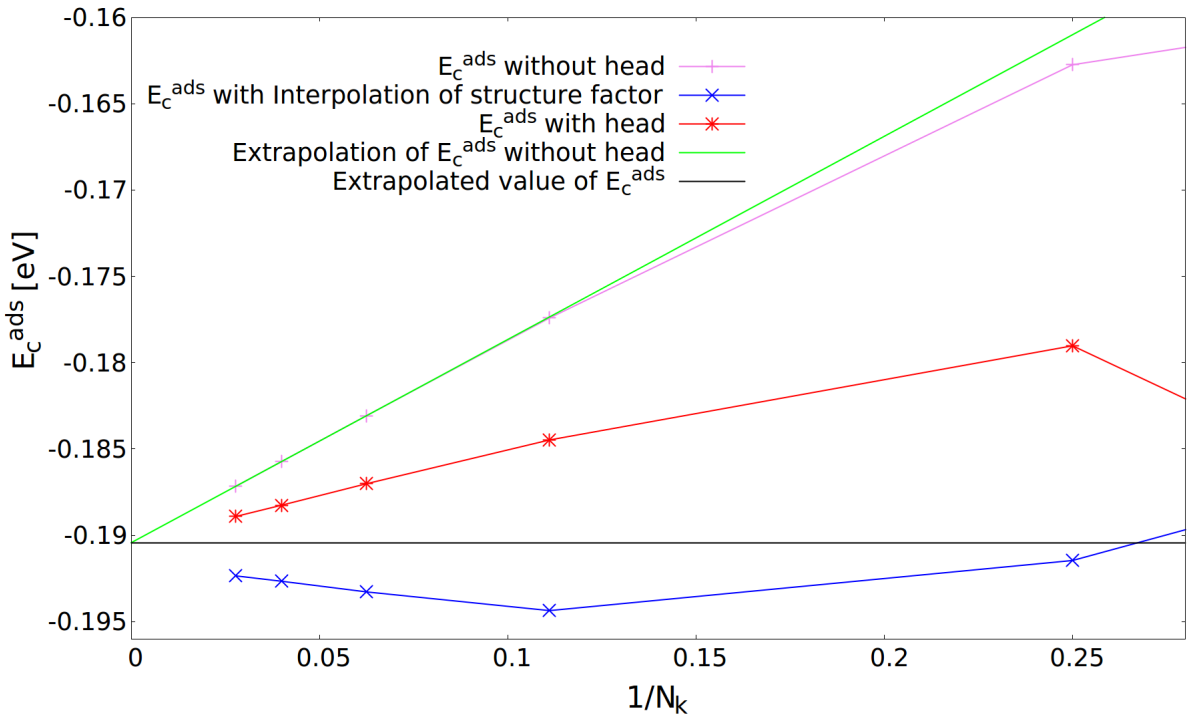


Figure 12: The figure depicts the convergence of the RPA correlation energy with an increasing number of k-points for the adsorption of water on boron nitride. The fastest convergence of E_c is obtained by interpolation of the structure factor.

Tricubic interpolation of the structure factor improves the convergence of the RPA

correlation energy for the adsorption of water on boron nitride. Changes in the correlation energy of less than 1 meV can be observed for a k-point mesh of $4 \times 4 \times 1$ or finer. Including head contributions has a similar effect, however, a k-point mesh of $5 \times 5 \times 1$ needs to be chosen to yield the same accuracy.

7 Conclusion

In this thesis, an algorithm for tricubic spline interpolation was developed and implemented in the VASP code. It was used to interpolate the electronic structure factor, which is needed to calculate the RPA correlation energy in equation (137). The interpolation was tested for different systems including both insulators and semiconductors. In addition, the effect of the interpolation was also tested for the adsorption of water on boron nitride.

It was shown that the interpolation leads to a faster convergence of the RPA correlation energy for all materials that were investigated. Simultaneously, the computational effort of the interpolation is far less than the effort to compute exact values of the structure factor at finer grids. This makes it possible to use coarser k-point meshes with subsequent interpolations of the structure factor instead of refining the k-point mesh which would lead to a high computational effort.

In the future, the proposed interpolation technique needs to be applied to even more systems in order to assess its viability.

In this Master's thesis, the interpolation procedure was used only for the RPA. However, it is possible to perform the same procedure for other ab initio methods such as Møller-Plesset perturbation theory (MP). The analytical form of the structure factor will change, depending on what kind of approximation is chosen. Very similar work has already been done using the Coupled Cluster ansatz (CC) in [19].

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8 Appendix

The following Python program was used to perform the ACFDT-RPA calculations. The four seperate steps are highlighted.

```
import os
import sys
import os.path

#-----------------------------------------------------------------------------
# routine for RPA calculation C2
#-----------------------------------------------------------------------------
cores=sys.argv[1]
vasp_command=["vasp_tricubic_std",".vts"]
#vasp_command=["vasp",".v"]
data1="POSCAR"
data2="INCAR"
data3="OUTCAR"

KPAR="KPAR = 2"
ALGOEX="ALGO = Exact"
ALGOEIG="ALGO = EIGENVAL"
ALGOACFDT="ALGO = ACFDT"
PRECFOCK="PRECFOCK = Fast"
LWAVE="LWAVE = .FALSE."
LOPTICS="LOPTICS = .FALSE."
LPEAD="LPEAD = .FALSE."
LHFCALC="LHFCALC = .TRUE."
NELM="NELM = 1"
AEXX="AEXX = 1.0"
NMAXFOCKAE="NMAXFOCKAE = 1"
LMAXFOCKAE="LMAXFOCKAE = 4"
NOMEGA="NOMEGA = 8"
EDIFF="EDIFF = 1E-8"

#-----------------------------------------------------------------------------
#FIRST CALCULATION STEP
#-----------------------------------------------------------------------------

#CREATE INCAR FILE FOR FIRST VASP RUN
os.system("cat INCAR.bak > INCAR")
os.system("rm WAVECAR WAVEDER")
g=open(data2, "a")
g.write(str(KPAR)+'\n'+str(EDIFF))
g.close()

#FIRST VASP RUN
```

```
os.system("mpirun -np "+str(cores)+str(" ")+str(vasp_command[0]))

#SAVE DATA FROM FIRST VASP RUN
os.system("cat INCAR POSCAR KPOINTS OUTCAR > OUTCAR.DFT"+str(vasp_command[1]))

#SEARCH FOR "MAXIMUM NUMBER OF PLANE-WAVES" IN FIRST OUTCAR FILE
h=open(data3, "r")
for line in h:
  if "maximum number of" in line:
    NBTOT=int((int(line.split()[4])+int(cores)-1)/int(cores))*int(cores)
NBANDS="NBANDS = "+str(NBTOT)

#REMOVE INCAR FILE
os.system("rm INCAR")

#-------------------------------------------------------------------------------
#SECOND CALCULATION STEP
#-------------------------------------------------------------------------------

#CREATE INCAR FILE FOR SECOND VASP RUN
os.system("cat INCAR.bak > INCAR")
g=open(data2, "a")
g.write(str(KPAR)+'\n'+str(LWAVE)+'\n'+str(LHFCALC)+'\n'+str(NELM)+
'\n'+str(AEXX)+'\n'+str(ALGOEIG)+'\n'+str(PRECFOCK)+'\n'+str(LMAXFOCKAE)+
'\n'+str(NMAXFOCKAE))
g.close()

#SECOND VASP RUN
os.system("mpirun -np "+str(cores)+str(" ")+str(vasp_command[0]))

#SAVE DATA FROM SECOND VASP RUN
os.system("cat INCAR POSCAR KPOINTS OUTCAR > OUTCAR.DFT.HF"+str(vasp_command[1]))

#REMOVE INCAR FILE
os.system("rm INCAR")

#-------------------------------------------------------------------------------
#THIRD CALCULATION STEP
#-------------------------------------------------------------------------------

#CREATE INCAR FOR THIRD VASP RUN
os.system("cat INCAR.bak > INCAR")
g=open(data2, "a")
g.write(str(KPAR)+'\n'+str(NBANDS)+'\n'+str(LOPTICS)+'\n'+str(LPEAD)
+'\n'+str(NELM)+'\n'+str(ALGOEX))
g.close()
```

```
#THIRD VASP RUN
os.system("mpirun -np "+str(cores)+str(" ")+str(vasp_command[0]))

#SAVE DATA FROM THIRD VASP RUN
os.system("cat INCAR POSCAR KPOINTS OUTCAR > OUTCAR.DFT.DIAG"+str(vasp_command[1]))

#REMOVE INCAR FILE
os.system("rm INCAR")

#-------------------------------------------------------------------------------
#FOURTH CALCULATION STEP
#-------------------------------------------------------------------------------

#CREATE INCAR FOR FOURTH VASP RUN
os.system("cat INCAR.bak > INCAR")
g=open(data2, "a")
g.write(str(PRECFOCK)+'\n'+str(NBANDS)+'\n'+str(ALGOACFDT)+'\n'+str(NOMEGA)+
'\n'+str(KPAR))
g.write(str(PRECFOCK)+'\n'+str(NBANDS)+'\n'+str(ALGOACFDT)+'\n'+str(NOMEGA))
g.close()

#FOURTH VASP RUN
os.system("mpirun -np "+str(cores)+str(" ")+str(vasp_command[0]))

#SAVE DATA FROM FOURTH VASP RUN
os.system("cat INCAR POSCAR KPOINTS OUTCAR > OUTCAR.ACFDT"+str(vasp_command[1]))

#REMOVE INCAR FILE
os.system("rm INCAR")

os.system("rm OUTCAR")
```