



DISSERTATION / DOCTORAL THESIS

Titel der Dissertation / Title of the Doctoral Thesis

**Ab-initio description of optical properties of semiconductors and
nanocrystals**

verfasst von / submitted by
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angestrebter akademischer Grad / in partial fulfilment of the requirements for the degree of
Doktor der Naturwissenschaften (Dr. rer. nat.)

Wien, 2017 / Vienna, 2017

Studienkennzahl lt. Studienblatt /
degree programme code as it appears
on the student record sheet:

A 796 605 411

Dissertationsgebiet lt. Studienblatt /
field of study as it appears
on the student record sheet:

Physik

Betreut von / Supervisor:

Univ.-Prof. Dipl.-Ing. Dr. Georg Kresse

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Notation

Abbreviations

HK	Hohenberg-Kohn
DFT	Density functional theory
TDDFT	Time-dependent density functional theory
BSE	Bethe-Salpeter equation
SEQ	Schrödinger equation
AE	All-electron
PP	Pseudopotential
QP	Quasiparticle
TE	Time evolution

General notation

$\hbar$	Planck's constant divided by 2π
m_e	electron mass
$\mathbf{r}$	position variable
σ	spin variable
$\mathbf{x}$	$\mathbf{r}\sigma$
Ψ	N-particle wave function
$\mathbf{k}$	wave vector of the 1st Brillouin zone
$\mathbf{k}_F$	Fermi wave vector
r_s	Wigner-Seitz radius
$\hat{\psi}$	field operator
$[\hat{A}, \hat{B}]$	$\hat{A}\hat{B} - \hat{B}\hat{A}$

1. Introduction

One of the major milestones in physics is clearly the introduction of quantum mechanics, i.e. the transition from classical description of particles into the corresponding description of wave fields. The classical trajectory in real space of a rigid particle is substituted by its quantum mechanical counterpart, namely the probability distribution, as given due to the square of the amplitude of the corresponding wave. Although the tools of quantum mechanics allow to treat physical phenomena on a microscopic scale exactly, its application already beyond the simple hydrogen problem reveals first issues. For multi-electron systems, may it be atoms, molecules or solids the electronic many-particle wave function is unknown and simplified approximations within in a single particle picture have been suggested, such as by Hartree or later by Fock who introduced a first kind of correlation due to the exclusion principle for fermionic particles. The biggest challenge for many-particle systems, though is still the proper description of the collective motion of the particles that is traditionally summarized as correlation. Although there is a variety of methods to tackle the solution of the many-particle problem the question about the validity still remains. A feedback on the theoretical results can only be given by comparison to results that are available by experiments. In particular, spectroscopic investigations allow to draw conclusions about the electronic structure and the closely connected excitation properties. In this context, the conceptual idea of Landau [3] and his introduction of quasiparticles being excited states of a many-particle system bridges the gap between spectroscopy and theoretical forecasts. The accessible quantity at this stage is the spectral function with its pronounced peaks on the energy scale that can be related to quasiparticle energies. Moreover, this function can be calculated through the Green's function formalism which is the method of choice to calculate excitation energies. In this work, we are, however, less interested in excitations that are caused by e.g. (inverse) photoemission or energy loss spectroscopy, but rather in neutral excitations. From the experimental point of view, one is faced with the process of photo absorption due to impinging radiation on a macroscopic sample. The involved process generates a polarization of the medium due to the promotion of a valence electron into the unoccupied manifold and hence leads to the formation of electron-hole pairs. Their description is even more involved as it requires to solve a four-point integral equation for the polarization function, commonly known as the Bethe-Salpeter equation. In the realm of perturbation theory, Hedin's set of coupled integro-differential equations[4, 5] introduces not only the one-particle Green's function but also the polarization function and in turn allows to calculate quasiparticle energies as well as optical excitation energies. As these equations are footed on a purely quantum mechanical treatment, the numerical implementation results in so-called *ab-initio* methods and are thus free of any parametric assumptions. With the aid of these methods a rigorous description of real materials may be achieved and pave the way to predict materials properties a priori that might become

interesting for industrial applications. Setting the focus on optical absorption spectra, as it is done in this thesis, the main motivation has been pinned down to calculate optical excitation energies by a less expensive method than solving the Bethe-Salpeter equation[6]. Although this method yields excellent agreement with experimental results, its huge computational work load constrains its application to system with only few atoms. For ideal crystal structures, this is easily manageable, and the compute time can be tuned to a moderate limit by the number of $\mathbf{k}$ -points. Concerning the field of photovoltaics, a mono-crystalline sample is rather difficult to produce and cheap commercial solar cells are usually amorphous. Due to the lower symmetry, the resulting unit cell has to comprise a large number of atoms to adequately simulate an amorphous crystal structure. This in turn induces a much larger number of transition pairs (electron-hole pairs) that are necessary to calculate the underlying polarization function and thus again displays the limiting factor for this kind of calculations. It is therefore desirable to have a method that yields exactly the results from the solution of the Bethe-Salpeter equation but with an improved scaling with respect to the system size.

The present thesis aims to present the theoretical background in order to integrate the desired calculation of excitation energies. In the first part 2, I touch briefly the concept of density functional theory, as it serves as the common method to calculate the Kohn-Sham orbitals and energies. These quantities are the natural ingredients for the subsequent calculation of quasi-particle energies and corresponding orbitals. Their derivation in terms of the Green's function formalism is presented in chapter 3. Additionally, I have included the topic of Feynman diagrams to enrich the discussion on how to calculate the one-particle Green's function different from Hedin's approach. In the upcoming chapter 4, the discussion on the density response function is set up, as it is the central quantity from which the macroscopic dielectric function can be calculated. In particular, the imaginary part is of interest, since it yields the desired optical absorption spectrum within the long wave length limit. It is followed by a brief introduction on time-dependent density functional theory as this method will be compared to the time evolution of orbitals presented in the last chapter. The second last part 7 is devoted to the question in what way the commonly applied Tamm-Dancoff approximation influences the optical absorption spectrum as compared to the full solution of the Bethe-Salpeter equation. Results are given for selected bulk materials such as silicon, carbon and lithium fluoride and for the lithium fluoride dimer molecule. Additionally, the inclusion of a finite momentum transfer for the dielectric function beyond the long wave length limit is presented for silicon. The last chapter 8 is devoted to the time evolution of orbitals as an equivalent method to calculate the dielectric macroscopic function. Within the time-dependent density functional theory, this method is benchmarked in terms of its computational efficiency. To compare with, the Casida method is chosen, as this method is algebraic equivalent to the solution of the polarization function from the BSE.

2. Density functional theory

The description of the many-particle Hamiltonian and hence the solution of the electronic wave function belongs to one of the many challenging tasks in solid state theory. In this chapter I am introducing density functional theory, which opened the route to go beyond the classical description of the electronic interaction, i.e. the Hartree term and the exact exchange term. The primary concept of DFT is to answer the question in what way the electronic ground state of a many-particle system can be calculated from a ground state density. If there is a unique relation between the density and the wave function, it implies their equivalence and hence transforms the many-body wave function to be a function of the density. The solution to this ambiguous problem was given by the Hohenberg-Kohn theorems [7] which hold the tenet of this theory. It proves that the exact treatment of any ground state property is solely given by the ground state density.

2.1. Basic ideas

Before Hohenberg and Kohn formulated their concept of the density functional theory, several attempts have been made to set up a density based theory. Among them are the works of Thomas[8] and Fermi[9], the work of Dirac[10] and that of Weizsäcker[11]. All of these theories have been developed in a short period of time, while Thomas and Fermi independently developed the fundamental concept of density functional theory, although they were not aware about this by that time. Without going into detail, the crucial quantity within the Thomas-Fermi theory is the total energy of an atom expressed solely in terms of the one-particle density. This ansatz is based on the assumption of a dense and homogenous distribution of non-interacting electrons around the atom and allows to approximate the kinetic energy as a functional of the density. The resulting energy functional then consists of the approximated kinetic energy term, the electron-electron repulsion term and the attracting core-electron term. However, the simplification of the electronic distribution around the atom results in an unphysical behaviour of the resulting density for very short and large distances [12] and does not allow to describe the binding of molecules [13]. Corrections to the Thomas-Fermi theory have been suggested e.g. by Weizsäcker to account for effects of an inhomogeneous density by adding a density gradient correction to the approximated kinetic energy term. Another missing part was added by Dirac who integrated an approximated and local expression for the exchange energy term. However, none of these early developed density based theories are capable to properly describe total atomic energies and lead to unphysical behaviour for negatively charged ions [12]. From the current point of view of density functional theory, it is well known that effects of correlation and exchange manifestly improves not only the description of atoms and molecules but also that of extended systems. Nevertheless,

the aforementioned theories pioneered the development of modern density functional theory by introducing a density based energy functional and concomitantly evoked the question for admissible densities. These questions have been answered by Hohenberg and Kohn who gave evidence that any ground state property can be calculated from the knowledge of the ground state density alone. Thus, the density instead of the wave function acts as the basic variable and consequently one needs to answer the question, whether a N -particle ground state wave function Ψ_N can be obtained from a given density ρ_N . This is the central problem of DFT, and the first Hohenberg-Kohn theorem proves this one to one correspondence between both quantities, i.e. $\Psi_N \leftrightarrow \rho_N$.

2.2. The Hohenberg-Kohn theorems

The following discussion is based on a fermionic N -particle system described by a non-relativistic and time independent Hamiltonian $\hat{H}$ of the form

$$\hat{H} = \hat{T}_e + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}}. \quad (2.1)$$

In the equation above the kinetic energy operator for the electrons $\hat{T}_e$ is given by

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2. \quad (2.2)$$

The potential term $\hat{V}_{\text{int}}$ describes the electronic Coulomb interaction,

$$\hat{V}_{\text{int}} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.3)$$

and the external potential $\hat{V}_{\text{ext}}$ accounts for any interactions between the electrons and the nuclei and has a general local form

$$\hat{V}_{\text{ext}} = \sum_i V_{\text{ext}}(\mathbf{r}_i). \quad (2.4)$$

From the knowledge of the full Hamiltonian $\hat{H}$, the many-body wavefunction is fully determined and hence the corresponding density ρ_N . However, the external potential is still not yet defined and should be chosen so that $\hat{H}$ has a non-degenerated ground state. With this restriction for the external potential the first Hohenberg-Kohn theorem states:

Hohenberg-Kohn Theorem 1. *The external potential $V_{\text{ext}}(\mathbf{r})$ for an interacting many-body system is uniquely defined, except for a constant shift, by the ground state density.*

The proof of this theorem is given by the inverse of the consecutive mapping $(CD)^{-1}$, whereas

C and D are defined as the following:

$$\begin{aligned} C : \mathcal{V} &\mapsto \mathcal{W} \quad \text{with} \quad \mathcal{V} := \left\{ V_{\text{ext}}(\mathbf{r}) \mid \hat{H} \text{ has a non-degenerated ground state} \right\} \\ &\quad \text{and} \quad \mathcal{W} := \left\{ \Psi_N \mid \text{is a } N\text{-particle ground state wave function} \right\} \\ D : \mathcal{W} &\mapsto \mathcal{D} \quad \text{with} \quad \mathcal{D} := \left\{ \rho_N \mid \text{is a density to a } N\text{-particle ground state} \right\}. \end{aligned}$$

Both mappings C and D are surjective, since for every external potential the corresponding Schrödinger equation always yields a ground state Ψ_N which eventually is associated to a density ρ_N . What remains is to proof the existence of the inverse mapping $(CD)^{-1}$ that is, given if C and D are both surjective and injective. The injectivity of C induces that two different external potentials $V_{\text{ext}}(\mathbf{r})$ and $V'_{\text{ext}}(\mathbf{r})$ lead to two different ground states Ψ_N and Ψ'_N , respectively. Under the condition that both external potentials differ by more than a constant shift, i.e. $V_{\text{ext}} \neq V'_{\text{ext}} + \text{const.}$, the corresponding Schrödinger equations

$$\hat{T} + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} |\Psi_N\rangle = E_{\text{gs}} |\Psi_N\rangle \quad (2.5)$$

$$\hat{T} + \hat{V}_{\text{int}} + \hat{V}'_{\text{ext}} |\Psi'_N\rangle = E'_{\text{gs}} |\Psi'_N\rangle \quad (2.6)$$

lead to a contradiction by assuming that V_{ext} and V'_{ext} yield the same ground state, i.e. $\Psi_N = \Psi'_N$. Subtracting Eq.(2.6) from Eq.(2.5) one obtains the relation

$$V_{\text{ext}} - V'_{\text{ext}} = E_{\text{gs}} - E'_{\text{gs}} \quad (2.7)$$

that refutes the condition on the two external potentials. Thus the mapping C is proven additionally to be injective and is therefore also bijective. The injectivity of the map D follows the same line of arguments and one needs to show that two different ground states Ψ_N and Ψ'_N yield two different densities ρ_N and ρ'_N , respectively. By the Rayleigh-Ritz theorem, the expectation value of the Hamiltonian $\langle \Psi | \hat{H} | \Psi \rangle$ becomes stationary, if Ψ is an eigenvector of $\hat{H}$ and takes its minimum at the ground state Ψ_N . Thus the following inequality holds

$$E_{\text{gs}} = \langle \Psi_N | \hat{T}_e + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} | \Psi_N \rangle < \langle \Psi'_N | \hat{T}_e + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} | \Psi'_N \rangle \quad (2.8)$$

assuming Ψ'_N to be not the ground state of $\hat{H}$. The last term of Eq.(2.8) can be rewritten in the following manner,

$$E_{\text{gs}} < \langle \Psi'_N | \hat{T}_e + \hat{V}_{\text{int}} + \hat{V}'_{\text{ext}} + \hat{V}_{\text{ext}} - \hat{V}'_{\text{ext}} | \Psi'_N \rangle = E'_{\text{gs}} + \int d\mathbf{r} \rho'(\mathbf{r}) (V_{\text{ext}} - V'_{\text{ext}}). \quad (2.9)$$

If one considers the ground state energy to be E'_{gs} , one arrives at the same equation, i.e. Eq.(2.9),

¹In order to obtain this relation, one notes that the external potentials are multiplicative operators in real space and the wave functions are assumed to be square integrable, i.e. $\langle \Psi_N | \Psi_N \rangle > 0$.

²One assumes orthogonal ground state wave function: $\langle \Psi_N | \Psi_N \rangle = 1$ and $\langle \Psi'_N | \Psi'_N \rangle = 1$

with the primed and unprimed quantities now being interchanged,

$$E'_{\text{gs}} < \langle \Psi_N | \hat{T}_e + \hat{V}_{\text{int}} + \hat{V}_{\text{ext}} + \hat{V}'_{\text{ext}} - \hat{V}_{\text{ext}} | \Psi_N \rangle = E_{\text{gs}} + \int d\mathbf{r} \rho(\mathbf{r}') (V'_{\text{ext}} - V_{\text{ext}}). \quad (2.10)$$

In order to disprove that two different ground states yield the same density, i.e. $\rho_N = \rho'_N$, one adds up Eq.(2.9) and Eq.(2.10) and arrives at the final contradiction:

$$E_{\text{gs}} + E'_{\text{gs}} < E_{\text{gs}} + E'_{\text{gs}}. \quad (2.11)$$

Thus the mapping D between the set of ground state wave functions and the set of corresponding densities is also additionally injective and hence bijective. Since the mappings C and D are invertible the inverse mapping $(CD)^{-1}$ equals the consecutive mapping $D^{-1}C^{-1}$. In other words, from a given ground state density the external potential is uniquely defined and the first Hohenberg-Kohn theorem is proven. $\square$

As a direct consequence, the ground state density uniquely defines the full hamiltonian $\hat{H}$ and thus determines any state Ψ_N that is associated to the corresponding Schrödinger equation with the hamiltonian $\hat{H}$. Up to now, the first HK-theorem gives no prescription how to calculate the ground state density, and it gives no answer how to solve the many-body problem in the presence of an external potential. However, the Hohenberg-Kohn theorem implies due to the inverse mapping D^{-1} that the expectation value of an observable, and in particular the total energy E , is a functional of the ground state density. This establishes the variational character of the HK-theorem, since the resulting energy functional to a given external potential $\tilde{V}_{\text{ext}}$, defined by

$$E_{\tilde{V}}[\rho] := \langle \Psi[\rho] | \hat{T} + \hat{V}_{\text{int}} + \tilde{V}_{\text{ext}} | \Psi[\rho] \rangle, \quad (2.12)$$

takes its minimum value, the ground state energy, at the ground state density $\tilde{\rho}$ corresponding to the external potential $\tilde{V}_{\text{ext}}$. This allows to solve for the ground state density by minimizing the functional $E_{\tilde{V}}[\rho]$:

$$E_{\text{gs}} = \min_{\rho \in \mathcal{D}} E_{\tilde{V}}[\rho] \quad \text{and} \quad E_{\text{gs}} \equiv E_{\tilde{V}}[\tilde{\rho}]. \quad (2.13)$$

The second HK-theorem states:

Hohenberg-Kohn Theorem 2. *For any external potential $V_{\text{ext}}(\mathbf{r})$ there exists a universal energy functional $E_{\text{HK}}[\rho]$ that is minimized by the exact ground state density ρ_N and takes its global minimum at the exact ground state energy.*

Since the ground state Ψ_N is a functional of the density so is the kinetic energy term and the Coulomb interaction term and allows to define the universal Hohenberg-Kohn functional F_{HK} ,

$$F_{\text{HK}}[\rho] := \langle \Psi[\rho] | \hat{T} + \hat{V}_{\text{int}} | \Psi[\rho] \rangle. \quad (2.14)$$

This functional is independent of the external potential and thus is universal in the sense that it is identical for all electron systems such as atoms, molecules and solids. The HK energy functional

now reads

$$E_{\text{HK}}[\rho] = F_{\text{HK}}[\rho] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}), \quad (2.15)$$

and takes its minimum value at the correct ground state density. If this functional is evaluated at a density ρ' different from the true ground state density one finds due to the Rayleigh-Ritz theorem the following relation

$$E_{\text{HK}}[\rho'] = F_{\text{HK}}[\rho'] + \int d\mathbf{r} V_{\text{ext}} \rho'(\mathbf{r}) > F_{\text{HK}}[\rho] + \int d\mathbf{r} V_{\text{ext}} \rho(\mathbf{r}) = E_{\text{HK}}[\rho], \quad (2.16)$$

which proves the second HK-theorem. Hence due to the Hohenberg-Kohn theorems the calculation of the (3N-dimensional) ground state wave function is mapped onto the (3-dimensional) ground state density by use of the Rayleigh-Ritz variational method.

In this context the question of the extensibility of the energy functional to possible degenerated ground states or the question of the representability of the ground state densities arise quite naturally. In the case of degenerated ground states the previous introduced mapping C does not exist any more, but its inverse. On the other hand one can still map the (degenerated) ground state onto a ground state density. Hence, there still exists a mapping between the ground state density and the corresponding external potential. The proof that two different external potentials (different by more than a constant) also yield two different ground states still holds for degenerated ground states. Additionally, two different ground states that belong to two different external potentials can only be associated to two different ground state densities. Thus the correspondence between the external potential and the ground state density is still established. However, the HK-energy functional needs to be extended to all ground state wave functions that lead to a given ground state density, since the inverse mapping D^{-1} is not valid. The question about the representability of ground state densities has been touched already in the original paper by Hohenberg and Kohn.³ As by construction of the HK-theorems, every density is so called *pure-state V-representable* and the theorem only guarantees the existence of not more than one external potential to a given density. However, this includes the case where no potential can be found. Hence the definition of dismissible and well-behaved⁴ ground state densities needs to be extended. A new class of densities haven been suggested by Levy[14] and Lieb[15] that includes densities that cannot be deduced by a *pure* ground state Ψ_N but a by an ensemble of ground states $\{\Psi_{N,i}\}$, described by the corresponding density matrix. The resulting density is then given by the trace of the density matrix $\hat{Q}$, i.e.

$$\rho_Q(\mathbf{r}) = \text{tr}\{\hat{Q}\hat{\rho}(\mathbf{r})\} = \sum_{i=1}^M c_i \rho_i(\mathbf{r})^5 \quad \text{with} \quad \hat{Q} = \sum_i c_i |\Psi_{N,i}\rangle \langle \Psi_{N,i}|^6 \quad (2.17)$$

³[7] [...]We cannot prove whether an arbitrary positive density distribution $n'(\mathbf{r})$, which satisfy the condition, $\int n'(\mathbf{r})d\mathbf{r} = \text{integer}$ can be realized by some external potential.[...]

⁴A well-behaved density is integrable, i.e. $\int d\mathbf{r}\rho(\mathbf{r}) < \infty$, and positive, i.e. $\rho(\mathbf{r}) > 0$ and continuously differentiable.

⁵From the density operator $\hat{\rho}(\mathbf{r})$, the density $\rho_i(\mathbf{r})$ is given by $\langle \Psi_{N,i} | \hat{\rho}(\mathbf{r}) | \Psi_{N,i} \rangle$.

⁶The coefficients obey the condition $\sum_i c_i = 1$ and $c_i = c_i^* \geq 0$.

and Eq.(2.17) shows that the density $\rho_Q(\mathbf{r})$ cannot be generated by just one (pure) ground state wave function but by an ensemble of ground state wave functions⁷. This class of densities is called *ensemble V-representable*. The related extension of the Hohenberg-Kohn functional to this class of densities requires to expand the set of possible ground state wave functions $\mathcal{W}$ to the set of density matrices $\hat{Q}$ due to a given external potential. Moreover, the associated densities are then obtained by Eq.(2.17). The proof of the first Hohenberg-Kohn theorem can be shown in a similar way as demonstrated for the *pure state V-representable* densities, i.e. the subspace of densities corresponding to two different external potentials $V_{\text{ext}}, V'_{\text{ext}}$ that differ by more than a constant is disjunct:

$$\mathcal{D}_V \cap \mathcal{D}_{V'} = \emptyset. \quad (2.18)$$

Since the ground state wave function is replaced by the density matrix one can define the extended Hohenberg-Kohn functional with respect to *ensemble V-representable* densities as the following

$$F_{\text{EHK}}[\rho] := \text{tr} \left\{ \hat{Q}[\rho] \left(\hat{T} + \hat{V}_{\text{int}} \right) \right\}. \quad (2.19)$$

With regard to Eq.(2.19) the density matrix $\hat{Q}[\rho]$ is uniquely connected to an external potential, which itself leads to a given *ensemble V-representable* density. Up to this stage the HK-functional has been defined for densities that are uniquely associated to an external potential. As shown by Englisch and Englisch [16], there exist densities which lead to singular external potentials and hence are not *ensemble V-representable*. This however conflicts the proof that every density on a discretized grid is *ensemble V-representable*. In this context Levy[17, 14] and Lieb[15] suggested their constrained search formulation with respect to the energy functional [Eq.(2.13)]. Instead of minimizing the energy functional with respect to the subspace of all *pure-state V-representable* densities one searches the minimum in the subspace of all antisymmetric and normalized wave functions that lead to a given density. The density itself is part of a set of non-negative densities subject to the constraint to integrate to the total number of particles. In a second step the resulting energy functional is minimized in the subspace of the aforementioned densities. Hence the ground state energy can be written as

$$E_{\text{gs}} = \inf_{\rho(\mathbf{r})} \left\{ F_{\text{LL}}[\rho] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \right\}, \quad (2.20)$$

where the Levy-Lieb functional is defined as

$$F_{\text{LL}}[\rho] := \inf_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{V}_{\text{int}} | \Psi \rangle. \quad (2.21)$$

One notes the important difference to the Hohenberg-Kohn functional, i.e. the expression by Levy and Lieb considers any density that is derivable from an antisymmetric wave function. Such densities are called *pure-state N-representable* and it has been shown that in principle every non-negative density can be constructed from a single Slater determinant[18]. As demonstrated by Levy[17], the functional F_{LL} equals the HK-functional F_{HK} for *pure-state V-representable*

⁷One assumes a set of orthogonal, linear independent and degenerated ground states $\Psi_{N,i}$.

densities since the energy functional

$$F_{\text{LL}}[\rho] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \quad (2.22)$$

satisfy the variational principle as it yields the ground state energy at the exact ground state density. With regard to the extended Hohenberg-Kohn functional, there also exist a corresponding functional, suggested by Lieb[19] and Valone[20], which searches the infimum in the subspace of density matrices which lead to a prescribed density.

2.3. Kohn-Sham equations

Due to the labouring expression of the mutual Coulomb interaction [Eq.(2.3)] it is desirable to circumvent the solution of the fully interacting many-body problem given by the Hamiltonian in Eq.(2.1). This idea proposed by Kohn and Sham [21] is based on the introduction of an auxiliary non-interacting system whose ground state density $\rho_{\text{gs},s}$ equals the ground state density ρ_{gs} of the interacting system. With this ansatz the resulting independent-particle problem can be solved exactly at the expense of a new quantity that accounts for all exchange and correlation effects. Due to the Hohenberg-Kohn theorems the density $\rho_{\text{gs},s}$ is then uniquely linked to a (local) effective one-particle potential $V_s(\mathbf{r})$. This is called *non-interacting V-representability*. Aiming to achieve a relation between the non-interacting problem subject to the potential V_s and the fully interacting problem one considers the energy functional of the non-interacting auxiliary system

$$E_s[\rho] = T_s[\rho] + \int d\mathbf{r} V_s(\mathbf{r})\rho(\mathbf{r}) = T_s[\rho] + E_{\text{eff}}[\rho], \quad (2.23)$$

with the kinetic energy functional $T_s[\rho]$ of independent particles. The variation of Eq.(2.23) with respect to the density and subject to the constraint of a fixed particle number N becomes stationary at the non-interacting ground state density $\rho_{\text{gs},s}(\mathbf{r})$, i.e.

$$\frac{\delta}{\delta\rho(\mathbf{r})} \left[E_s[\rho] - \mu_s \int d\mathbf{r} \rho(\mathbf{r}) \right]_{\rho=\rho_{\text{gs},s}} = \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} \Big|_{\rho=\rho_{\text{gs},s}} + V_s(\mathbf{r}) - \mu_s = 0, \quad (2.24)$$

and yields the solution for the effective single-particle potential up to a constant μ_s

$$V_s(\mathbf{r}) - \mu_s = - \frac{\delta T_s[\rho]}{\delta\rho(\mathbf{r})} \Big|_{\rho=\rho_{\text{gs},s}}. \quad (2.25)$$

The knowledge of V_s allows to write the corresponding Schrödinger equation for the non-interacting system in the form of

$$\left[-\frac{\hbar^2}{2m} \nabla_{\mathbf{r}}^2 + V_s(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}). \quad (2.26)$$

So far the kinetic energy functional $T_s[\rho]$ is by construction only defined on the domain of *non-interacting V-representable* densities. In order to map the interacting system onto the non-interacting system, the right hand side of Eq.(2.25) must also hold for densities of an interacting

system. By claiming this assumption to be true, it remains to find an alternative expression for the energy functional $E_s[\rho]$ in order to capture the total energy of the fully interacting system. As already shown by Hohenberg and Kohn [7] it is advantageous to separate additionally the Hartree energy term from the energy functional [Eq.(2.15)] that is then stated as

$$E_V[\rho] = T_s[\rho] + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r})v(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}') + E_{\text{XC}}[\rho]. \quad (2.27)$$

The introduced exchange and correlation energy is, by comparison with Eq.(2.15), given by

$$E_{\text{XC}}[\rho] = F_{\text{HK}}[\rho] - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r})v(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}') - T_s[\rho] \quad (2.28)$$

and includes the difference between the kinetic energy of the true interacting system and that of the non-interacting system. Additionally, it also needs to take into account self-interaction corrections that appear due to the Hartree energy term. The relation of the exchange-correlation energy to the Kohn-Sham energy functional is now established by

$$\begin{aligned} E_{\text{XC}}[\rho] &= E_{\text{eff}}[\rho] - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r})v(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}') - \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) \\ &= E_s[\rho] - T_s[\rho] - \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r})v(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}') - \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}). \end{aligned} \quad (2.29)$$

Hence it is clear that by Eq.(2.29) the effective potential V_s must account for all many-particle effects of exchange and correlation via a corresponding new potential, the exchange-correlation potential. To conclude the final calculation of the effective one-particle potential the variation of the energy functional [Eq.(2.27)] (of interacting particles) subject to the constraint of a fixed particle number needs to vanish at the exact ground state density ρ_{gs} as well, i.e.

$$\begin{aligned} 0 &= \frac{\delta}{\delta\rho} \left[E_V[\rho] - \mu' \int d\mathbf{r} \rho(\mathbf{r}) \right]_{\rho=\rho_{\text{gs}}} \\ &= \left[\frac{\delta T_s[\rho]}{\delta\rho} + V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r}') + V_{\text{xc}}[\rho](\mathbf{r}) \right]_{\rho=\rho_{\text{gs}}} - \mu \end{aligned} \quad (2.30)$$

At this point the exchange-correlation potential is defined as

$$V_{\text{xc}}[\rho](\mathbf{r}) := \frac{\delta E_{\text{xc}}[\rho]}{\delta\rho}. \quad (2.31)$$

Finally, the comparison of Eq.(2.25) and the right hand side of Eq.(2.30) allows to set the non-interacting potential V_s into relation to the interacting system under the assumption of the equivalence of the non-interacting and interacting ground state densities. One obtains up to a constant $\mu - \mu_s$:

$$V_s(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}')\rho_{\text{gs}}(\mathbf{r}') + V_{\text{xc}}[\rho_{\text{gs}}](\mathbf{r}) - (\mu - \mu_s). \quad (2.32)$$

The crucial point is the existence of the kinetic energy functional for *interacting* V -representable densities for which different extensions exist [22]. However, functional differentiability has been proven only by Lieb [15] where the ground state density is searched from within a set of ensembles of antisymmetric wave functions that lead to a prescribed density. In that sense, the kinetic energy functional in Eq.(2.30) needs to be replaced by the corresponding Lieb extension $T_s^L[\rho]$:

$$T_s^L[\rho] = \inf_{\hat{Q} \rightarrow \rho} \text{tr}\{\hat{Q}\hat{T}\}. \quad (2.33)$$

With Eq.(2.32) and Eq.(2.26) the Schrödinger equation is completely determined. By occupying the N lowest energetic states, i.e. $\varepsilon_1 \leq \varepsilon_2 \leq \dots \leq \varepsilon_N$, the corresponding ground state density is given by

$$\rho_{\text{gs}}(\mathbf{r}) = \rho_{\text{gs},s}(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2 \quad (2.34)$$

and concludes the Kohn-Sham equations. Since the single particle wave functions $\varphi_i(\mathbf{r})$ determine the effective potential $V_s(\mathbf{r})$, which itself determines the orbitals $\varphi_i(\mathbf{r})$, the Kohn-Sham equations have to be solved self-consistently. This can be done iteratively with a guess of an initial density, which is then updated iteratively. The iteration cycle terminates if the iteratively calculated density equals the ground state density or the density at iteration n has reached a convergence criterium. With the aid of the ground state density ρ_{gs} one obtains the ground state energy. From the solution of the Kohn-Sham equations the non-interacting kinetic energy term can be rewritten from Eq.(2.23) and Eq.(2.32) as

$$T_s[\rho_{\text{gs}}] = \sum_{i=1}^N \varepsilon_i - \int d\mathbf{r} V_{\text{ext}}(\mathbf{r})\rho_{\text{gs}}(\mathbf{r}) - \int d\mathbf{r}' \rho_{\text{gs}}(\mathbf{r})v(\mathbf{r} - \mathbf{r}')\rho_{\text{gs}}(\mathbf{r}') - \int d\mathbf{r} V_{\text{xc}}(\mathbf{r})\rho_{\text{gs}}(\mathbf{r}) \quad (2.35)$$

and further one obtains the final expression for the ground state energy by substituting $T_s[\rho]$ from Eq.(2.35) in Eq.(2.27)

$$E_V[\rho_{\text{gs}}] = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int d\mathbf{r}' \rho_{\text{gs}}(\mathbf{r})v(\mathbf{r} - \mathbf{r}')\rho_{\text{gs}}(\mathbf{r}') - \int d\mathbf{r} V_{\text{xc}}(\mathbf{r})\rho_{\text{gs}}(\mathbf{r}) + E_{\text{xc}}[\rho_{\text{gs}}](\mathbf{r}). \quad (2.36)$$

2.4. The exchange-correlation functional

By virtue of the Kohn-Sham approach, the introduced exchange-correlation functional is a priori unknown and requires further consideration. In this section, I will make use of the concept of the reduced density matrix. It formally allows to rewrite the total energy E_Ψ of a given N -particle system Ψ_N in terms of the first-order and second-order reduced density matrix. In consequence, the introduction of the so called exchange-correlation hole then allows to give an explicit expression for E_{xc} .

2.4.1. Exchange-correlation hole and pair distribution function

The description of a quantum mechanical N -particle state is uniquely given by the density operator $\hat{Q}$. For a pure state Ψ_N , the density operator is simply the projection operator $|\Psi_N\rangle\langle\Psi_N|$, from which in the spatial representation the spin-averaged density matrix of first and second order may be defined[23]:

$$\rho_1(\mathbf{r}'_1, \mathbf{r}_1) = N \sum_{\sigma_1} \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi_N(\mathbf{r}'_1 \sigma_1 \mathbf{x}_2 \dots \mathbf{x}_N) \Psi_N^*(\mathbf{r}_1 \sigma_1 \mathbf{x}_2 \dots \mathbf{x}_N) \quad (2.37)$$

$$\begin{aligned} \rho_2(\mathbf{r}'_1 \mathbf{r}'_2, \mathbf{r}_1 \mathbf{r}_2) &= \frac{N(N-1)}{2} \sum_{\sigma_1, \sigma_2} \int d\mathbf{x}_3 \dots d\mathbf{x}_N \Psi_N(d\mathbf{r}'_1 \sigma_1 d\mathbf{r}'_2 \sigma_2 d\mathbf{x}_3 \dots d\mathbf{x}_N) \times \\ &\quad \Psi_N^*(\mathbf{r}_1 \sigma_1 \mathbf{r}_2 \sigma_2 \mathbf{x}_3 \dots \mathbf{x}_N). \end{aligned} \quad (2.38)$$

Since the expectation value of any observable can be expressed in terms of the density operator, the total energy E_Ψ is given by

$$E_\Psi = \text{tr} \left(\hat{Q} \hat{H} \right), \quad (2.39)$$

where the trace is evaluated in terms of an arbitrary set of orthogonal basis vectors. With Eq.(2.1) we then obtain in the continuous basis of the position space

$$\begin{aligned} E_\Psi &= -\frac{\hbar^2}{2m_e} \int d\mathbf{r}_1 [\nabla_{\mathbf{r}_2}^2 \rho_1(\mathbf{r}_1, \mathbf{r}_2)]_{\mathbf{r}_1=\mathbf{r}_2} \\ &\quad + \int d\mathbf{r} V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) + \iint d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1 - \mathbf{r}_2) \rho_2(\mathbf{r}_1, \mathbf{r}_2). \end{aligned} \quad (2.40)$$

By inspection of the last term in Eq.(2.40), which is the electron-repulsion term, $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ is the diagonal element of the second order reduced density matrix [Eq.(2.38)], i.e. $\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_2(\mathbf{r}_1 \mathbf{r}_2, \mathbf{r}_1 \mathbf{r}_2)$. It simply yields the joint probability to find an electron at point $\mathbf{r}_1$ and simultaneously a second electron at point $\mathbf{r}_2$. For an uncorrelated N -particle system, $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ reduces to the product of one-particle densities $\frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2)$. Hence it is plausible to introduce a new quantity, the pair correlation function $h(\mathbf{r}_1, \mathbf{r}_2)$, which accounts for all correlation effects. Thus we can rewrite the diagonal matrix element $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ by [23]

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1, \mathbf{r}_2)]. \quad (2.41)$$

The electron-electron interaction term is now separated into the classical Hartree-term and a second part that incorporates the nonclassical correlation effects

$$V_{\text{int}} = \frac{1}{2} \left[\int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) v(\mathbf{r}_1 - \mathbf{r}_2) + \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) v(\mathbf{r}_1 - \mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) \right]. \quad (2.42)$$

Evenmore, the second term in Eq.(2.42) allows for a pictorial representation, namely the Coulomb interaction of an electron at point $\mathbf{r}_1$ with its surrounding exchange-correlation hole defined as,

$$\rho_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2). \quad (2.43)$$

It further obeys the following sum rule

$$\int d\mathbf{r}_2 \rho_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) = -1, \quad (2.44)$$

which holds for all points $\mathbf{r}_1$. This means that the exchange-correlation hole has a net electron charge just with opposite sign and describes the depletion of electrons around one particular electron due to the effects of Pauli repulsion (exchange). Usually, the term in Eq.(2.42) involving the pair-correlation function is called exchange-correlation energy. It can be calculated by use of the adiabatic connection theorem [24]. By tuning the electron-electron interaction with a parameter λ in the range of $0 \leq \lambda \leq 1$, the transition from a non-interacting system with eigenstate Ψ^0 into a fully interacting system with corresponding eigenstate Ψ^1 is induced. Every intermediate state Ψ^λ is an eigenstate to the corresponding Hamiltonian

$$\hat{H}^\lambda = \hat{T} + \lambda \hat{V}_{\text{int}} + \hat{V}_{\text{ext}}^\lambda. \quad (2.45)$$

Simultaneously, the external potential V_{ext}^λ scales in a way, so that the density for every λ remains unchanged, i.e.

$$\rho^\lambda(\mathbf{r}) = \langle \Psi^\lambda | \hat{\rho} | \Psi^\lambda \rangle = \rho(\mathbf{r}). \quad (2.46)$$

The existence of V_{ext}^λ is, however, not proven and is just an assumption. By means of the adiabatic connection we notice that the first HK-theorem is satisfied, since to every density ρ^λ an external potential V_{ext}^λ exists. Secondly, the total energy of the interacting N -particle system, as given by Eq.(2.15) can be calculated as

$$E_V[\rho] = \langle \Psi^1 | \hat{H} | \Psi^1 \rangle = \langle \Psi^0 | \hat{H} | \Psi^0 \rangle + \int_0^1 d\lambda \frac{\partial}{\partial \lambda} \langle \Psi^\lambda | \hat{H}^\lambda | \Psi^\lambda \rangle. \quad (2.47)$$

With the aid of the Hellman-Feynman Theorem [25, 26], the expectation value in the last term of Eq.(2.47) yields

$$\frac{\partial}{\partial \lambda} \langle \Psi^\lambda | \hat{H}^\lambda | \Psi^\lambda \rangle = \langle \Psi^\lambda | \frac{\partial}{\partial \lambda} \hat{H}^\lambda | \Psi^\lambda \rangle. \quad (2.48)$$

By exploiting Eq.(2.45) and Eq.(2.48) one obtains

$$\begin{aligned} E_V[\rho] &= \langle \Psi^0 | \hat{H} | \Psi^0 \rangle + \int_0^1 d\lambda \langle \Psi^\lambda | \hat{V}_{\text{int}} | \Psi^\lambda \rangle + \int d\mathbf{r} \rho(\mathbf{r}) \{ V_{\text{ext}}^1(\mathbf{r}) - V_{\text{ext}}^0(\mathbf{r}) \} \\ &= \langle \Psi^0 | \hat{T}_s | \Psi^0 \rangle + \int_0^1 d\lambda \langle \Psi^\lambda | \hat{V}_{\text{int}} | \Psi^\lambda \rangle + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}^1(\mathbf{r}). \end{aligned} \quad (2.49)$$

Comparing this expression with that of Eq.(2.27) one finds

$$\begin{aligned}
E_{\text{xc}}[\rho] &= \int_0^1 d\lambda \langle \Psi^\lambda | \hat{V}_{\text{int}} | \Psi^\lambda \rangle - \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1) v(\mathbf{r}_1 - \mathbf{r}_2) \rho(\mathbf{r}_2) \\
&= \iint d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1 - \mathbf{r}_2) \bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2) - \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1) v(\mathbf{r}_1 - \mathbf{r}_2) \rho(\mathbf{r}_2) \\
&\stackrel{(2.41)}{=} \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1 - \mathbf{r}_2) \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) \bar{h}(\mathbf{r}_1, \mathbf{r}_2) \\
&\stackrel{(2.43)}{=} \frac{1}{2} \iint d\mathbf{r}_1 d\mathbf{r}_2 v(\mathbf{r}_1 - \mathbf{r}_2) \rho(\mathbf{r}_1) \bar{\rho}_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2) \\
&:= \int d\mathbf{r}_1 \rho(\mathbf{r}_1) \epsilon_{\text{xc}}(\mathbf{r}_1),
\end{aligned} \tag{2.50}$$

where the coupling-constant averaged two-particle density $\bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2)$ is introduced by

$$\bar{\rho}_2(\mathbf{r}_1, \mathbf{r}_2) = \int_0^1 d\lambda \rho_2^\lambda(\mathbf{r}_1, \mathbf{r}_2), \tag{2.51}$$

and analogously $\bar{h}(\mathbf{r}_1, \mathbf{r}_2)$ and $\bar{\rho}_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2)$. The exchange-correlation energy per electron $\epsilon_{\text{xc}}(\mathbf{r})$ is then readily obtained from Eq.(2.50) by

$$\epsilon_{\text{xc}}(\mathbf{r}_1) = \frac{1}{2} \int d\mathbf{r}_2 v(\mathbf{r}_1 - \mathbf{r}_2) \bar{\rho}_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2). \tag{2.52}$$

Hence, a proper approximation of $E_{\text{xc}}[\rho]$ relies on the analysis of the averaged exchange-correlation hole $\bar{\rho}_{\text{xc}}$. As shown by Gunnarsson and Lundqvist [27], any contributions to the exchange-correlation energy can be calculated from the spherical average of the exchange-correlation hole, obeying the sum rule of Eq.(2.44). This is a stringent constraint test for any possible approximations for $\bar{\rho}_{\text{xc}}$.

2.4.2. Local density approximation

The question for a reasonable expression of the exchange-correlation energy, clearly depends on the approximation of the spatial distribution of the charge density ρ . A remarkably working approximation of E_{xc} has been suggested by Kohn and Sham in their pioneering work [21] where the density is assumed to vary 'slowly' along the Wigner-Seitz radius r_s . Based on this premise, ϵ_{xc} is approximated at the point $\mathbf{r}$ by the corresponding exchange-correlation energy per electron of an homogenous electron gas with the density at that point $\mathbf{r}$:

$$E_{\text{xc}}[\rho] \approx E_{\text{xc}}^{\text{LDA}}[\rho] = \int d\mathbf{r} \epsilon_{\text{xc}}^{\text{hom}}[\rho(\mathbf{r})] \rho(\mathbf{r}). \tag{2.53}$$

For the homogenous electron gas, the exchange energy per electron ϵ_x^{hom} can be calculated analytically, and it remains to find approximative solutions of the correlation part ϵ_c^{hom} ⁸. Several

⁸The xc energy per particle can be split up into a correlation part and an exchange part, i.e. $\epsilon_{\text{xc}}^{\text{hom}} = \epsilon_c^{\text{hom}} + \epsilon_x^{\text{hom}}$.

methods have been suggested to determine ϵ_c^{hom} . Very early, Wigner[28] estimated the correlation part for the homogenous electron gas by a simple interpolation scheme between the limits of high-densities and low-densities. An exact expression has been given by Gell-Mann and Bruckner[29] in the limiting case of high densities ($r_s \rightarrow 0$) by use of a perturbative treatment of ϵ_c^{hom} w.r.t. r_s . Further approaches are that by Hedin and Lundqvist within the random phase approximation [30], a parameter-based ansatz by Gunnarsson and Lundqvist[27], as well as results from quantum Monte Carlo calculations[31] that have been used to extrapolate ϵ_c^{hom} to high or low densities[32]. The success of the LDA is however surprising, since in real solids, the condition of a slowly varying density is hardly complied. The reason of the success is two-fold. On the one hand, the exchange-correlation hole ρ_{xc}^{LDA} fulfills the sum rule from Eq.(2.44). On the other hand, ρ_{xc}^{LDA} is spherical symmetric and hence it suffices to describe the true exchange-correlation hole for a homogenous electron gas exactly.

2.4.3. Generalized-gradient approximation

In order to account for density gradients in $E_{xc}[\rho]$, Kohn and Sham suggested the so-called gradient expansion approximation (GEA)[21]. The idea behind the GEA is to expand the xc-functional $E_{xc}[\rho]$ about the uniform density in a Taylor series, where the leading term is given by $E_{xc}^{\text{LDA}}[\rho]$. An explicit derivation can be found e.g. in Ref.[33]. Since the GEA is based on slowly varying densities it does not lead to significant improvements upon the LDA, as it cannot describe properly rapidly varying densities in real solids. In particular, the associated exchange-correlation hole ρ_{xc}^{GEA} disobeys the sum rule (2.44). To avoid the short-comings of the GEA, the generalized-gradient approximation introduces a general expression for $E_{xc}[\rho]$ in the form of

$$E_{xc}^{\text{GGA}}[\rho] = \int d\mathbf{r} f(\rho(\mathbf{r}), \nabla\rho(\mathbf{r})). \quad (2.54)$$

Hereby, the function f is an analytic function that usually depends on several parameters subject to meet exact conditions for the exchange-correlation hole. Those conditions are e.g. the negativity of the exchange hole ρ_x or the sum rule of Eq.(2.44). For spin-unpolarized systems, f may be written as [34]

$$E_{xc}^{\text{GGA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \epsilon_x^{\text{hom}}(\rho(\mathbf{r})) F_{xc}(r_s, s(\mathbf{r})) \quad (2.55)$$

where F_{xc} is the enhancement factor over local exchange and $s(\mathbf{r})$ is the dimensionless reduced density gradient, which in first order reads

$$s_1 = \frac{|\nabla\rho|}{2k_F\rho}. \quad (2.56)$$

There exist several forms for the exchange part F_x of Eq.(2.55), e.g. the aforementioned GEA, the form of Perdew and Wang [35] or the form of Becke[36], who gave an expression to capture the long range Coulomb interaction of an electron with its surrounding exchange hole including gradient corrections. These functionals describe the exchange energy equally for slowly varying

density gradients, however, they show different behaviour at large density gradients. A good reason to include the density gradient not only to the exchange hole but also to the correlation hole is that the resulting xc-hole becomes more localized around an electron[34]. This in turn improves the description of the xc-hole close to the electron if higher density gradient contributions, i.e. s_m are taken into account. The downside of this approach is the worsened description of the xc-hole at larger distances. Therefore, a possible solution is to truncate the long range contribution of ρ_{xc} in real space and introduce a generalized-gradient approximation for the xc-hole for any order of s [34]. In this work we use the PBE-GGA functional[37] which considers density gradients of first order s_1 . It treats the correlation energy and exchange energy in the following form

$$E_c^{\text{PBE-GGA}}[\rho_\uparrow, \rho_\downarrow] = \int d\mathbf{r} \rho(\mathbf{r}) \left[\epsilon_c^{\text{hom}}(r_S, \xi) + H(r_S, \xi, t) \right] \quad (2.57)$$

$$\xi = \frac{\rho_\uparrow - \rho_\downarrow}{\rho} \quad \text{and} \quad t = \frac{|\nabla \rho|}{2k_s \rho}$$

$$E_x^{\text{PBE-GGA}}[\rho_\uparrow, \rho_\downarrow] = \frac{1}{2} \left\{ \int d\mathbf{r} \rho_\uparrow(\mathbf{r}) \epsilon_c^{\text{hom}}(2\rho_\uparrow(\mathbf{r})) F_x(s_1) + \int d\mathbf{r} \rho_\downarrow(\mathbf{r}) \epsilon_c^{\text{hom}}(2\rho_\downarrow(\mathbf{r})) F_x(s) \right\}. \quad (2.58)$$

In Eq.(2.57), several expressions for the correlation hole of the homogenous electron gas ϵ_c^{hom} exist as given in section (2.4.2). To account for the effects of density gradients in the correlation energy, a second reduced density gradient t is introduced. It is a measure of the density variation over the screening length k_s , the characteristic length scale at which correlation between an electron and its surrounding hole effectively occurs and is not completely screened.

3. Green's function approach

Despite the success of the density functional theory, for a rigorous description of the electronic problem, governed by the Hamiltonian (2.1), the full quantum mechanical problem, i.e. the Schrödinger equation needs to be solved. This task is a basket case considering the number of atoms of about 10^{23} in a real material and thus makes the exact representation of the many-particle wave function impossible. Nevertheless, the method of the quantization of wave fields provides another approach to the many-body problem and recasts it in terms of an operator-like description. I follow the description of Ref.[38].

3.1. Second quantization

The many-problem boils down to the solution of the stationary many-particle Schrödinger equation

$$\hat{H} |\Psi\rangle = E |\Psi\rangle \quad (3.1)$$

with the Hamiltonian of the electronic problem [Eq.(2.1)]. The conceptual idea of second quantization is to convert a one-particle theory into a many-particle theory. Correspondingly, the one-particle wave function ψ is regarded as a classical field obeying a one-particle Schrödinger equation

$$\left[-\frac{\hbar}{2m_e} \nabla_{\mathbf{r}}^2 + V_{\text{ext}}(\mathbf{r}) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}). \quad (3.2)$$

In order to quantize the field ψ , the method of Hamilton's least action for classical particles is applied. Hereby, one may think of cutting down the entire field ψ into small subvolumes $\delta V^{(s)}$ and associate the canonical coordinates $q_j \rightarrow \psi^{(s)}$ ¹ to the averaged field in the subvolume s [38]. Hence the Lagrangian L takes the form $L = \sum_s \delta V^{(s)} \mathcal{L}^{(s)}$. From the variation principle, the action integral in the limiting case of infinitesimal cell volumes $\delta V^{(s)} \rightarrow 0$

$$I = \int_{t_1}^{t_2} L dt \quad (3.3)$$

becomes stationary if the variation δI vanishes. The resulting Euler-Lagrange equation for the field ψ then becomes

$$\frac{d}{dt} \frac{\delta L}{\delta \dot{\psi}} - \frac{\delta L}{\delta \psi} = 0^2 \quad (3.4)$$

¹The corresponding velocities $\dot{q}_j$ are then given by $\dot{\psi}^{(s)}$.

²The conjugated momentum π is defined as $\frac{\delta L}{\delta \dot{\psi}}$ and equals $-\frac{\hbar}{i} \psi^*$ since the Hamiltonian H is just the expectation value of the Hamilton operator in Eq.(3.2).

from which the equation of motion for the field ψ , i.e. the time-dependent Schrödinger equation might be obtained. With the Lagrangian density $\mathcal{L} = \lim_{\delta V^{(s)} \rightarrow 0} \mathcal{L}^{(s)}$ and the conjugated momentum π the Hamiltonian H , given by

$$H = \int d\mathbf{r} \left[\pi \dot{\psi} - \mathcal{L} \right] \quad (3.5)$$

allows to replace the field equations (3.4) by the corresponding canonical field equations $\dot{\psi} = \frac{\delta H}{\delta \pi}$ and $\dot{\pi} = \frac{\delta H}{\delta \psi}$. The quantization of the wave field is now obtained by postulating the commutation rules [39, 40]

$$[\psi(\mathbf{r}), \psi(\mathbf{r}')] = [\pi(\mathbf{r}), \pi(\mathbf{r}')] = 0 \quad [\pi(\mathbf{r}), \psi(\mathbf{r}')] = \frac{\hbar}{i} \delta(\mathbf{r} - \mathbf{r}') \quad (3.6)$$

which transform the field ψ and the conjugated momentum π into hermitian operators. This approach is known as *second quantization*. Eventually, the connection between the one-particle SEQ to the many-particle SEQ is obtained, by expanding the classical wave field or respectively the field operator by a complete and orthonormal basis set $\{\varphi_j\}$. Writing

$$\hat{\psi}(\mathbf{r}) = \sum_j \hat{a}_j \varphi_j(\mathbf{r}) \quad (3.7)$$

$$\hat{\psi}^\dagger(\mathbf{r}) = \sum_j \hat{a}_j^\dagger \varphi_j^*(\mathbf{r}), \quad (3.8)$$

the Hamiltonian of Eq.(3.5), becomes an Hermitian operator within the second quantization (sq) formulation

$$\hat{H}_{0,\text{sq}} = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}) \left[-\frac{\hbar}{2m_e} \nabla_{\mathbf{r}} + V_{\text{ext}}(\mathbf{r}) \right] \hat{\psi}(\mathbf{r}) \quad (3.9)$$

that is defined in the space of all N -particle Hilbert spaces $\mathcal{H}_N$ that constitute the Fock space $\mathcal{H}_{\text{Fock}}$:

$$\mathcal{H}_{\text{Fock}} := \bigoplus_{N=0}^{\infty} \mathcal{H}_N \quad \text{and} \quad \mathcal{H}_N = \bigotimes_{i=1}^N \mathcal{H}_1. \quad (3.10)$$

To account for the indistinguishability of the particles one needs to restrict $\mathcal{H}_N$ to the subspaces of completely symmetric (bosons) or antisymmetric (fermions) N -particle Hilbert spaces, i.e. $\mathcal{H}_N^+$ and $\mathcal{H}_N^-$. Every state vector of the corresponding Hilbert space $\mathcal{H}_N^\nu$ ³ is build up from the vacuum state $|0\rangle$ as the following:

$$|n_{\mathbf{r}_1} n_{\mathbf{r}_2} \dots n_{\mathbf{r}_N}\rangle \equiv |\mathbf{r}_1 \mathbf{r}_2 \dots \mathbf{r}_N\rangle_\nu = \frac{1}{\sqrt{\prod_l n_l!}} \psi^\dagger(\mathbf{r}_1) \psi^\dagger(\mathbf{r}_2) \dots \psi^\dagger(\mathbf{r}_N) |0\rangle. \quad (3.11)$$

The real space basis vectors defined by Eq.(3.11) allow to construct any N -particle state by a linear combination of the same. In the case of a fermionic N -particle state, the commutation rules [Eq.(3.6)], however, do not obey the Pauli exclusion principle and hold only for bosons. Thus, the commutation rules for the fermionic field operators require a modification, i.e. they

³For bosons we have $\nu = +$ and $\nu = -$ for fermions.

⁴The variable n_l counts the number of particles that occupy the same quantum state. For fermions it is simply 0 or 1. The index ν at the second ket vector denotes the a complete (anti)symmetrized N -particle state.

need to anticommute:

$$[\psi(\mathbf{r}), \psi(\mathbf{r}')]_+ = [\psi^\dagger(\mathbf{r}), \psi^\dagger(\mathbf{r}')]_+ = 0 \quad [\psi(\mathbf{r}), \psi^\dagger(\mathbf{r}')]_+ = \delta(\mathbf{r} - \mathbf{r}'). \quad (3.12)$$

The Hamilton operator as defined in Eq.(3.9) includes the one-particle operators of the kinetic energy and that of the external potential in second quantization representation. In general, an arbitrary N -particle operator in the subspace of $\mathcal{H}_N^\nu$ is represented by

$$\begin{aligned} \hat{O}_N(t) = & \frac{1}{N!} \int d\mathbf{r}'_1 \dots \int d\mathbf{r}'_N \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N \langle \mathbf{r}'_1 \dots \mathbf{r}'_N | \hat{O}_N(t) | \mathbf{r}_1 \dots \mathbf{r}_N \rangle \times \\ & \times \hat{\psi}^\dagger(\mathbf{r}'_1) \dots \hat{\psi}^\dagger(\mathbf{r}'_N) \hat{\psi}(\mathbf{r}_1) \dots \hat{\psi}(\mathbf{r}_N).^5 \end{aligned} \quad (3.13)$$

Taking into account the explicit representation of the Coulomb interaction [see appendix (B)], $\hat{H}_{0,\text{sq}}$ is easily extendable to include the electron-electron interaction to become the Hamiltonian of an interacting many-particle system

$$\hat{H}_{\text{sq}} = \hat{H}_{0,\text{sq}} + \hat{V}_{\text{int},\text{sq}}. \quad (3.14)$$

Within the one-particle subspace $\mathcal{H}_1^\nu$, Eq.(3.14) simply reduces to the one-particle Hamilton operator [Eq.(3.9)]. Hence, for $N > 1$ $\hat{H}_{\text{sq}}$ accounts for all particle-particle interactions. Therefore, the transition from a one-particle to a many-particle theory is formally established and one can exploit the anticommutation rules beneficially to obtain a rigorous expansion of the electron-electron interactions, which will be demonstrated in the next section. The introduction of the field operators $\hat{\psi}$ is given here in the Schrödinger picture. However, for practical applications, the Heisenberg picture is more desirable since the dynamics of the wave function is now transferred to the operators by a unitary transformation:

$$\hat{\psi}(\mathbf{r}, t) = e^{\frac{i}{\hbar} \hat{H}_{\text{sq}} t} \hat{\psi}(\mathbf{r}) e^{-\frac{i}{\hbar} \hat{H}_{\text{sq}} t}.^6 \quad (3.15)$$

Thereby, the anticommutation rules [Eq.(3.12)] remain unchanged, if the field operators are taken at the same time t and the entire dynamic, formerly described by the time dependent SEQ, is now carried by the operators that obey the equation of motion in the Heisenberg picture

$$\frac{d}{dt} \hat{O}_N = \frac{1}{i\hbar} [\hat{H}, \hat{O}_N] + \frac{\partial}{\partial t} \hat{O}_N(t). \quad (3.16)$$

3.2. The quasiparticle concept

The determination of physical properties of interest is very often treated by the principle of *actio* and *reactio*. In the context of the electronic properties and thus the solution of the many-body problem, solving the many-body SEQ, the quasiparticle concept plays an essential role. From the perspective of an experimental access, probing a system and watch its response is a state-of-the-art procedure, to obtain the desired informations. The perturbation of an arbitrary electronic

⁶ $\hat{H}_{\text{sq}}$ is the full Hamilton operator containing any kind of interactions.

system goes along with an excitation of the same. Hence, excitation energies will be measured and give a first insight about the physical processes. Assuming the electronic many-particle system to be non-interacting, the excitation energy, i.e. the energy difference with and without one extra particle added to the system, would yield the electronic energy level of that extra particle. This process is known as indirect photoemission and would measure the electronic density of unoccupied states. Clearly, the inverse process, then measures the density of occupied states. Although the interactions among the electrons cannot be neglected, the idea of non-interacting particles can be carried over to interacting particles by introducing a new kind of particle, which is the *quasiparticle*. Such a particle is considered as a stable and long-lived excitation of a many-particle system, as it is then also measurable by experiment. In the picture of the direct or indirect photoemission the added electron or hole will be shielded by the electrons in the vicinity and thus becomes a 'dressed' particle. This concept goes back to Landau's Fermi liquid theory [41, 42, 43], who introduced the quasiparticle in the framework of the adiabatic evolution. By adiabatically switching on the interaction among the particles plus the extra particle, the quantum states remain unchanged which allows a one-to-one correspondence between the non-interacting and interacting Fermi system. A necessary condition to observe a quasiparticle state is that its life time is larger than the adiabatic switch-on time, which becomes infinite for a strict adiabatic process. In turn, an infinite life time corresponds to an ideal non-interacting quasiparticle and the problem of the full interaction would have been decoupled into the solution of an independent one-particle problem. For practical purposes however, one needs to find reasonable quasiparticles, whose interaction is small enough to be treated in a perturbative manner. Besides these single-particle excitations, the particle concept holds for any kind of excitations in a many-particle systems, such as phonons, plasmons or excitons. In particular, the latter one belongs to the elementary excitation of collective modes, which is a measure of the density fluctuation due to an external probe⁷. With the aid of the quantum field theory, a rigorous description of a quasiparticle can be established and allows for a systematic, even though approximate, solution to the many-body problem.

3.3. Green's function - definition

3.3.1. Propagators

Motivated by the picture of the 'dressed' particle being injected into the many-particle system, one may ask about its countless interactions with the surrounding particles and which 'track' this particular particle may take. This notion of a quasiparticle then can be expressed in terms of an electron propagator $G^>$ or hole propagator $G^<$. For spin-unpolarized systems one defines [44]:

$$G^>(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \frac{1}{i\hbar} \langle \hat{\psi}_{\sigma_1}(\mathbf{r}_1 t_1) \hat{\psi}_{\sigma_2}^\dagger(\mathbf{r}_2 t_2) \rangle \delta_{\sigma_1, \sigma_2} \quad (3.17)$$

$$G^<(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = -\frac{1}{i\hbar} \langle \hat{\psi}_{\sigma_2}^\dagger(\mathbf{r}_2 t_2) \hat{\psi}_{\sigma_1}(\mathbf{r}_1 t_1) \rangle \delta_{\sigma_1, \sigma_2}. \quad (3.18)$$

⁷Plasmons being collective modes as well, but due to correlation effects among the particles.

Due to the delta function in the definition for the propagators above, they become spin independent and I will drop the spin index from now on. The expectation value of the product of field operators in Eq.(3.17) and Eq.(3.18) is defined in terms of the density or statistical operator $\hat{\rho}$. To account for finite temperatures T and a variable particle number N , we may define $\hat{\rho}$ within the grand canonical ensemble, i.e.

$$\hat{\rho} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\text{tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}\}} \quad \text{and} \quad \beta = \frac{1}{k_B T}, \quad (3.19)$$

where k_B is the Boltzmann constant and μ denotes the chemical potential, which accounts for the particle exchange of the thermodynamical systems with the environment. Since the Hamiltonian $\hat{H}$ and the particle operator $\hat{N}$ commute, they have the same basis of eigenfunctions $\{|m\rangle\}$, and the ensemble average $\langle \dots \rangle$ is then given by

$$\langle \hat{O} \rangle = \text{tr}\{\hat{\rho} \hat{O}\} = \sum_m \hat{\rho}_m \langle m | \hat{O} | m \rangle \quad \text{and} \quad \hat{\rho} | m \rangle = \rho_m | m \rangle. \quad (3.20)$$

In the zero-temperature limit, the statistical operator becomes the unity operator $\mathbb{1}$ and only the ground state Ψ_0 is fully occupied. Hence, Eq.(3.20) simplifies to

$$\lim_{T \rightarrow 0} \langle \hat{O} \rangle = \langle \Psi_0 | \hat{O} | \Psi_0 \rangle. \quad (3.21)$$

Finally, the definition of the electron and hole propagator allows for a simple interpretation, namely as a probability amplitude. It yields the probability to find an electron at the time point t_1 and the spatial point $\mathbf{r}_1$ if an electron has been added to the system at an earlier time t_2 and place $\mathbf{r}_2$ with both particles having the same spin orientation⁸. Obviously, the electron propagator describes the propagation of an added electron in positive time direction, i.e. $t_2 \rightarrow t_1$, while the hole propagates backward in time. Both propagators may be combined to ultimately define the *causal* or *time-ordered* Green's function

$$\begin{aligned} G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &:= \Theta(t_1 - t_2) G^>(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) + \Theta(t_2 - t_1) G^<(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \\ &:= \frac{1}{i\hbar} \langle \mathcal{T} \hat{\psi}(\mathbf{r}_1 t_1) \hat{\psi}^\dagger(\mathbf{r}_2 t_2) \rangle, \end{aligned} \quad (3.22)$$

with $\mathcal{T}$ denoting Wick's time ordering operator.

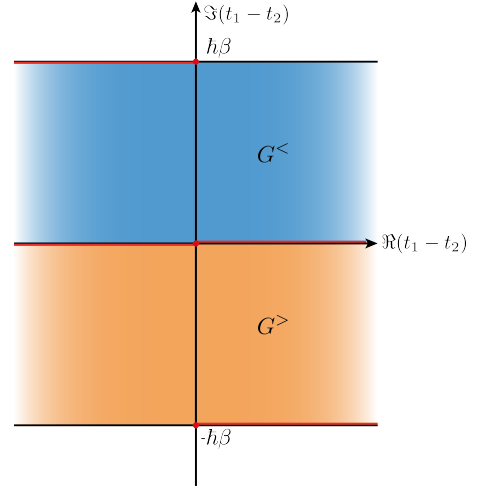
3.3.2. Spectral properties

The Fourier transform of the electron and hole propagator as shown in appendix E [Eq.(E.3) and Eq.(E.4)] allow for a representation of the Green's function [Eq.(3.22)] in the frequency domain in form of a Lehmann representation

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lim_{\eta \rightarrow 0} \frac{i}{2\pi} \int d\omega' \frac{G^>(\mathbf{r}_1, \mathbf{r}_2; \omega')}{\omega - \omega' + i\eta} - \frac{G^<(\mathbf{r}_1, \mathbf{r}_2; \omega')}{\omega - \omega' - i\eta}. \quad (3.23)$$

⁸The same interpretation also holds for the hole propagator according to its definition in Eq.(3.18).

Figure 3.1: Sketch of the complex time domain. The blue area shows the analytic region of the hole propagator $G^<$, while the orange part concerns the analytic region of the particle propagator $G^>$ respectively. The red lines and the red dots mark the non-analytic regions.



At least in the zero temperatur limit, i.e. $T \rightarrow 0$, a spectral representation of Eq.(3.23) might be derived

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lim_{\eta \rightarrow 0} \frac{1}{2\pi} \int d\omega' \frac{A(\mathbf{r}_1, \mathbf{r}_2; \omega')}{\omega - \omega' + i\eta \text{sgn}(\hbar\omega' - \mu)} \quad (3.24)$$

with the spectral weight function defined as

$$A(\mathbf{r}_1, \mathbf{r}_2; \omega) = i [G^>(\mathbf{r}_1, \mathbf{r}_2; \omega) - G^<(\mathbf{r}_1, \mathbf{r}_2; \omega)] \quad (3.25)$$

At finite temperatures, however, a regular spectral representation like Eq.(3.24) of the causal Green's function cannot be found. One obtains instead

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega' \left\{ \mathcal{P} \frac{1}{\omega - \omega'} - i\pi \delta(\omega - \omega') \tanh \frac{\beta}{2} (\hbar\omega' - \mu) \right\} A(\mathbf{r}_1, \mathbf{r}_2; \omega), \quad (3.26)$$

with the spectral weight function from Eq.(3.25). In order to obtain a spectral representation for the causal Green's function at finite temperatures, the Wick theorem is exploited[45]. While in the zero temperature limit the time differences are real, i.e. $(t_1 - t_2) \in \mathbb{R}$, they become complex otherwise¹⁰ as sketched in Fig.(3.1). On the complex time domain one finds a quasi-periodicity of $G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2)$ that is due to the relation of the electron and hole propagator:

$$G^<(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) = -e^{-\beta\mu} G^>(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2 - i\hbar\beta). \quad (3.27)$$

Equation (3.27) is the Martin-Schwinger relation [46] and connects both propagators on the entire complex time domain. A more detailed derivation is given in the appendix E. The causale Green's function thus is quasi periodic along the imaginary time axis within the intervall $|\Im(t_1 - t_2)| \leq \hbar\beta$,

⁹Here and in the following, μ denotes the chemical potential.

¹⁰For imaginary time differences, the theta function in Eq.(3.22) takes into account the imaginary part only, i.e. $\Theta[\Im(t_1 - t_2)]$.

and hence has a Fourier representation in the following form

$$G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) = -\frac{1}{i\hbar\beta} \sum_n \tilde{G}(\mathbf{r}_1, \mathbf{r}_2; z_n) e^{iz_n(t_1 - t_2)}. \quad (3.28)$$

The frequencies z_n are the fermionic Matsubara frequencies and are the poles of the Fermi-function. They allow for a simple spectral representation of the causal temperature dependent Green's function as

$$\tilde{G}(\mathbf{r}_1, \mathbf{r}_2; z_n) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \frac{A(\mathbf{r}_1, \mathbf{r}_2; \omega)}{z_n - \omega} \quad (3.29)$$

with the Matsubara frequencies

$$\hbar z_n = \mu - \frac{\pi n}{i\beta} \quad \text{with} \quad n = \pm 1, \pm 3, \pm 5, \dots \quad (3.30)$$

Considering the spectral representation [Eq.(3.29)], the Fourier transform may be continued to the entire complex plane, i.e. $z_n \rightarrow z$, except at the real frequency axis, and $\tilde{G}(z)$ coincides with $\tilde{G}(z_n)$ at the Matsubara frequencies. To conclude this section, two further Green's function, the retarded and advanced Green's function shall be mentioned at this point. They have, like the causal one the same physical content, but possess a spectral representation similar like Eq.(3.24) for all temperatures. While the retarded Green's function is analytical in the upper complex frequency plane, the advanced Green's function is analytical in the lower plane, respectively. Hence they can be obtained by approaching the real frequency axis either from above or below and one eventually finds the following relation:

$$G^{\text{ret/av}}(\mathbf{r}_1, \mathbf{r}_2, \omega) = \lim_{\eta \rightarrow 0^+} \tilde{G}(\mathbf{r}_1, \mathbf{r}_2, \omega \pm i\eta), \quad \omega \in \mathbb{R}. \quad (3.31)$$

Although both functions yield the exact excitation energies of the many-body system, it is only the causal Green's function that makes a perturbative series expansion possible.

3.4. Methods for determining the Green's function

As from the discussion of the previous sections, the Green's function is asked to incorporate the mutual particle interactions in the many-body system due to the additional injected electron or hole and is required additionally to yield information about the excitation energies or simply the quasiparticle energies. The term quasiparticle is a priori still unknown, but can be associated to pronounced peak structures in the spectral function. Both aspects shall be sketched in this section, following the references[60, 44, 48, 49].

3.4.1. Equation of motion for G

By inspecting the equation of motion for the field operators in the Heisenberg picture [Eq.(3.16)] one verifies by the time derivative of $G(t_1 - t_2)$ an equation of motion for the causal Green's

function that reads

$$\left[i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 - V_{\text{ion}}(\mathbf{r}_1) \right] G(1, 2) + i\hbar \int d3 v(1-3) G(1, 3, 2, 3^+) = \delta(1-2). \quad (3.32)$$

Some remarks are required at this point:

- the short hand notation $1 = \mathbf{r}_1 t_1$ is exploited
- the integral $d1$ abbreviates $\int d\mathbf{r}_1 \int dt_1$
- the external potential in the Hamiltonian of Eq.(3.16) is given by the local potential due to the nuclei $V_{\text{ion}}(\mathbf{r}_1)$
- the kernel of the Coulomb interaction is given by $v(1-2) \equiv \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta(t_1 - t_2)$
- the notation $1^+ = \mathbf{r}_1 t_1 - i\eta$ slightly shifts the time argument into the 'past', such that the time ordering operator $\mathcal{T}$ can be properly applied within the expression $G(1, 3, 2, 3^+)$

Obviously, the equation of motion for the causal Green's function involves a two-particle Green's function that is defined as

$$G(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \frac{1}{(i\hbar)^2} \left\langle \mathcal{T} \psi(\mathbf{r}_1 t_1) \psi(\mathbf{r}_2 t_2) \psi^\dagger(\mathbf{r}_4 t_4) \psi^\dagger(\mathbf{r}_3 t_3) \right\rangle. \quad (3.33)$$

Due to the fact that the (causal) one-particle Green's function requires the next higher order two-particle Green's function, which itself requires a three-particle Green's function for the corresponding equation of motion, an infinite hierarchy is successively generated. In order to break down this hierarchy, the equation of motion [Eq.(3.32)] can be formally rewritten by introducing the so-called *self-energy* Σ . With the aid of the inverse one-particle Green's function obeying the relation

$$\int d3 G(1, 3) G^{-1}(3, 2) = \int d3 G^{-1}(1, 3) G(3, 2) = \delta(1-2), \quad (3.34)$$

the self-energy may be defined as the following

$$\int d3 \Sigma(1, 3) G(3, 2) = -i\hbar \int d3 v(1-3) G(1, 3, 2, 3^+) \quad (3.35)$$

$$\Sigma(1, 2) = -i\hbar \int d3 d4 v(1-3) G(1, 3, 4, 3^+) G^{-1}(4, 2). \quad (3.36)$$

As a result, the equation of motion [Eq.(3.32)] reduces to the level of a one-particle description of the many-particle system

$$\left[i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 - V_{\text{ion}}(\mathbf{r}_1) \right] G(1, 2) - \int d3 \Sigma(1, 3) G(3, 2) = \delta(1-2), \quad (3.37)$$

where the self-energy contains the complete description of the many-particle interactions. Usually, one splits Σ into the classical Hartree term Σ_H

$$\Sigma_H(12) = -i\hbar \delta(1-2) \int d3 v(1-3)G(33^+) = \delta(1-2)V_H(\mathbf{r}_1)^{11} \quad (3.38)$$

and the remaining term Σ^{xc} , which includes now all exchange and correlation effects. Since neither the fully interacting Green's function nor the self-energy is known, a solution of Eq.(3.37) is a priori only possible through a non-interacting reference function $G_0(12)$, which has an explicit expression. Due to practical purposes, such a reference Green's function is chosen such as it already includes a fraction of the mutual electronic interactions. This might be incorporated by an exchange-correlation potential V_{xc}^{12} , which then results in a corresponding equation of motion for the non-interacting one-particle Green's function G_0

$$\left[i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 - V_{\text{ion}}(\mathbf{r}_1) - V_H(\mathbf{r}_1) \right] G_0(12) - \int d3 V_{xc}(13) G_0(32) = \delta(1-2). \quad (3.39)$$

Taking into account the separation of the Hartree term from Σ , Eq.(3.37) and Eq.(3.39) together, yield a self-consistent equation of motion of the one-particle Green's function in terms of its non-interacting counterpart

$$G(12) = G_0(12) + \int d3 d4 G_0(13) [\Sigma^{xc}(34) - V_{xc}(34)] G(42). \quad (3.40)$$

The equation above is also known as the *Dyson equation*.

3.4.2. Perturbative series expansion of G - zero temperature limit

The exact solution of the Dyson equation requires not only the knowledge of the complete description of the mutual electronic interaction, it also generates an infinite series of interaction terms for the self-energy. Such a series does not necessarily converge and it is common practice to find certain subseries in terms of Σ that summed up to infinity yields a converged but approximated solution to the Dyson equation. In the following, I restrict to the zero-temperature limit and follow the Refs. [50] and [51].

Adiabatic switch on procedure and Gell-Man and Low theorem

With the aid of the adiabatic switch on procedure the transition from a complete non-interacting eigenstate to the corresponding interacting state can be established. The electronic interaction is adiabatically switched on within the time intervall $[-\infty, 0]$ and switched off in the time intervall $[0, \infty]$, while the full interaction strength is reached by construction at the time point $t = 0$. By separating the many-body Hamiltonian Eq.(2.1) into a non-interacting part $\hat{H}_0$ and the remaining Coulomb interaction term $\hat{V}_{\text{int}}$ one introduces the adiabatic switch on procedure by an additional

¹¹The Hartree potential is given by the usual expression $V_H(\mathbf{r}_1) = \int d\mathbf{r}_3 v(\mathbf{r}_1 - \mathbf{r}_3)\rho(\mathbf{r}_3)$.

¹²We here assume a static and in general non-local potential, i.e. $V_{xc}(13) = v_{xc}(\mathbf{r}_1, \mathbf{r}_3)\delta(t_1 - t_3)$

exponential damping function as the following

$$\hat{H} = \hat{H}_0 + e^{-\xi|t|} \hat{V}_{\text{int}} \quad \text{and} \quad \xi \in \mathbb{R}^{\geq 0}. \quad (3.41)$$

Hence, in the limiting case $t \rightarrow -\infty$ the many-body state is just an eigenstate $|\Phi\rangle$ of the non-interacting Hamiltonian $\hat{H}_0$, which is equivalent in the Schrödinger picture as well as in the interaction picture. The latter one is usually the more appropriate picture to choose, since the corresponding time evolution operator $\hat{U}_{\text{I},\xi}$ then just contains the (possibly time dependent) interaction term $\hat{V}_{\text{int}}$. Thus the resulting many-body eigenstate $|\Psi\rangle$ at full interaction strength is then obtained by exploiting $\hat{U}_{\text{I},\xi}$ in the following way:

$$|\Psi_{\text{I}}(t_2 = 0)\rangle = \hat{U}_{\text{I},\xi}(t_2 = 0, t_1 = -\infty) |\Phi\rangle, \quad (3.42)$$

while the time evolution operator reads

$$\hat{U}_{\text{I},\xi}(t_2, t_1) = \sum_{l=0}^{\infty} \left(-\frac{i}{\hbar}\right)^l \frac{1}{l!} \int_{t_1}^{t_2} dt'_1 \dots \int_{t_1}^{t_2} dt'_l e^{-\xi(|t'_1| + \dots + |t'_l|)} \mathcal{T} [\hat{V}_{\text{int,I}}(t'_1) \dots \hat{V}_{\text{int,I}}(t'_l)].^{13} \quad (3.43)$$

The time ordering operator $\mathcal{T}$ appearing in the equation above is simply due to the iterative solution ansatz for the exact time evolution operator and arranges its arguments in descending time order. However, the adiabatic switch on procedure requires an infinitely slow transition from the non-interacting state to the corresponding interacting state. By inspection of Eq.(3.41), the limes $\xi \rightarrow 0$ has no physical meaning and diverges with ξ^{-1} [50]. Nevertheless, the theorem by Gell-Mann and Low [52] guarantees the existence of the limes

$$\lim_{\xi \rightarrow 0} \frac{\hat{U}_{\text{I},\xi}(0, -\infty) |\Phi\rangle}{\langle \Phi | \hat{U}_{\text{I},\xi}(0, -\infty) | \Phi \rangle} = \frac{|\Psi\rangle}{\langle \Phi | \Psi \rangle}, \quad (3.44)$$

while the rhs of Eq.(3.44) is an eigenstate of the full interacting Hamiltonian $\hat{H}$. It is the denominator in Eq.(3.44) that cancels the diverging phase in the nominator and thus allows for a finite expression of the ratio (lhs) to all orders in the perturbation series of the time evolution operator $\hat{U}_{\text{I},\xi}$.

Representation of G in a perturbation series and Wick's theorem

Following the definition of the causal Green's function, one finds the corresponding expression in the zero-temperature limit given by

$$G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \frac{1}{i\hbar} \langle \Psi_0 | \mathcal{T} \hat{\psi}(\mathbf{r}_1 t_1) \hat{\psi}^\dagger(\mathbf{r}_2 t_2) | \Psi_0 \rangle, \quad (3.45)$$

¹³The term $\hat{V}_{\text{int,I}}(t'_1)$ denotes the interaction operator within the interaction picture and is given by the unitary transformation $\hat{V}_{\text{int,I}}(t) = e^{\frac{i}{\hbar} \hat{H}_0 t} \hat{V}_{\text{int}} e^{-\frac{i}{\hbar} \hat{H}_0 t}$.

whereas Ψ_0 denotes the many-body ground state.¹⁴ Without loss of generality the rhs of Eq.(3.45) can be easily multiplied by a factor $\langle \Psi_0 | \Psi_0 \rangle^{-1} \frac{|\langle \Phi_0 | \Psi_0 \rangle|^2}{|\langle \Phi_0 | \Psi_0 \rangle|^2}$, assuming orthonormality of the ground state Ψ_0 . This extension now allows to rewrite the resulting denominator of Eq.(3.45), using Eq.(3.44), in the following way:

$$\begin{aligned} \frac{\langle \Psi_0 | \Psi_0 \rangle}{|\langle \Phi_0 | \Psi_0 \rangle|^2} &= \frac{\langle \Phi_0 | \hat{U}_{I,\xi}(\infty, 0) \hat{U}_{I,\xi}(0, -\infty) | \Phi_0 \rangle}{|\langle \Phi_0 | \Psi_0 \rangle|^2} \\ &= \frac{\langle \Phi_0 | \hat{S}_\xi | \Phi_0 \rangle}{|\langle \Phi_0 | \Psi_0 \rangle|^2}. \end{aligned} \quad (3.46)$$

On the other hand one obtains for the nominator of Eq.(3.45) the following expression:

$$\begin{aligned} &\frac{\langle \Phi_0 | \hat{U}_{I,\xi}(\infty, 0) \left\{ \hat{U}_{I,\xi}(0, t_1) \hat{\psi}_I(1) \hat{U}_{I,\xi}(t_1, 0) \right\} \left\{ \hat{U}_{I,\xi}(0, t_2) \hat{\psi}_I^\dagger(2) \hat{U}_{I,\xi}(t_2, 0) \right\} \hat{U}_{I,\xi}(0, -\infty) | \Phi_0 \rangle}{|\langle \Phi_0 | \Psi_0 \rangle|^2} \\ &= \frac{\langle \Phi_0 | \hat{U}_{I,\xi}(\infty, t_1) \hat{\psi}_I(1) \hat{U}_{I,\xi}(t_1, t_2) \hat{\psi}_I^\dagger(2) \hat{U}_{I,\xi}(t_2, -\infty) | \Phi_0 \rangle}{|\langle \Phi_0 | \Psi_0 \rangle|^2}. \end{aligned} \quad (3.47)$$

In the curly brackets, the field operators, previously given in the Heisenberg picture [see Eq.(3.45)], are now transformed into the interaction picture. The ordering of the time arguments t_1 and t_2 is captured by the time ordering operator appearing in the time evolution operator $\hat{U}_{I,\xi}$. From the ratio of Eq.(3.47) and Eq.(3.46) the causal Green's function takes the intermediate form

$$G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \frac{1}{i\hbar} \frac{\langle \Phi_0 | \hat{U}_{I,\xi}(\infty, t_1) \hat{\psi}_I(1) \hat{U}_{I,\xi}(t_1, t_2) \hat{\psi}_I^\dagger(2) \hat{U}_{I,\xi}(t_2, -\infty) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{S}_\xi | \Phi_0 \rangle} \quad (3.48)$$

which demonstrates the transition from the Heisenberg representation to the interaction picture. Evenmore, the limes $\xi \rightarrow 0$ can be performed, due to the construction of the interacting ground state Ψ_0 through the Gell-Mann and Low theorem. The final step comprises the substitution of the explicit expression for the time evolution operator $\hat{U}_{I,\xi}$ [Eq.(3.43)] into Eq.(3.48). After a lengthy derivation [see e.g.[50]], the nominator of equation (3.48) can be rewritten as a series expansion in terms of the Coulomb interaction $\hat{V}_{\text{int},I}$, i.e.

$$\begin{aligned} G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \frac{1}{i\hbar} \left\langle \Phi_0 \left| \sum_{l=0}^{\infty} \left(-\frac{i}{\hbar} \right)^l \frac{1}{l!} \int_{-\infty}^{\infty} dt'_1 \dots \int_{-\infty}^{\infty} dt'_l \right. \right. \\ &\quad \times \mathcal{T} \left\{ \hat{V}_{\text{int},I}(t'_1) \dots \hat{V}_{\text{int},I}(t'_l) \hat{\psi}_I(1) \hat{\psi}_I^\dagger(2) \right\} \left| \Phi_0 \right\rangle \\ &\quad \times \frac{1}{\langle \Phi_0 | \hat{S} | \Phi_0 \rangle}. \end{aligned} \quad (3.49)$$

¹⁴The Gell-Mann and Low theorem, however, does not necessarily imply that by switching on the Coulomb interaction, the resulting interacting eigenstate Ψ in Eq.(3.44) is also a ground state if Φ was ground state.

The Coulomb operator $\hat{V}_{\text{int,I}}(t)$ in the equation above is additionally expressed in second quantization [see also Eq.(B.1) in the appendix], i.e.

$$\hat{V}_{\text{int,I}}(t) = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \hat{\psi}_I^\dagger(\mathbf{r}_1, t) \hat{\psi}_I^\dagger(\mathbf{r}_2, t) v(\mathbf{r}_1 - \mathbf{r}_2, t) \hat{\psi}_I(\mathbf{r}_2, t) \hat{\psi}_I(\mathbf{r}_1, t), \quad (3.50)$$

so that the field operators $\hat{\psi}_I$ are the only type of arguments of the time ordering operator $\mathcal{T}$. In particular, the zero order term of the series expansion [Eq.(3.49)] just yields the non-interacting causal Green's function $G_0(1, 2)$ which reads

$$G_0(1, 2) = \frac{1}{i\hbar} \left\langle \Phi_0 \left| \mathcal{T} \hat{\psi}_I(1) \hat{\psi}_I^\dagger(2) \right| \Phi_0 \right\rangle. \quad (3.51)$$

This quantity can usually be calculated explicitly if a reference system of non-interacting particles is chosen. The corresponding orbitals form an orthogonal basis set $\{\varphi_\nu\}$ and allow to represent the non-interacting ground state $|\Phi_0\rangle$ as a single Slater determinant wave function. As we restrict to a fermionic many-body system, the orbitals φ_ν can be split into a spatial part $\varphi_\nu(\mathbf{r})$ and an additional spin part $f_\nu(\sigma)$, while the index ν comprises a complete set of single particle quantum numbers, such as the wave vector $\tilde{\mathbf{k}}$ and the spin component along the z -direction m_σ , which takes the values up $\uparrow$ and down $\downarrow$:

$$\varphi_\nu := \varphi_{\tilde{\mathbf{k}}, m_\sigma}(\mathbf{r}) f_{m_\sigma}(\sigma) \equiv \varphi_{\tilde{\mathbf{k}}, \sigma}(\mathbf{r}). \quad (3.52)$$

In consideration of a periodic lattice structure, the spatial part obeys the Bloch theorem [53] and consists of a plane wave modulated by a lattice periodic function $u_{\tilde{\mathbf{k}}}(\mathbf{r})$

$$\varphi_{\tilde{\mathbf{k}}, \sigma}(\mathbf{r}) = u_{n\mathbf{k}, \sigma}(\mathbf{r}) e^{i\tilde{\mathbf{k}}\mathbf{r}} \quad \text{and} \quad u_{n\mathbf{k}, \sigma}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}, \sigma}(\mathbf{r}). \quad (3.53)$$

Due to the lattice periodicity, the wave vector $\tilde{\mathbf{k}}$ in Eq.(3.53) can be restricted to a wave vector $\mathbf{k}$ that belongs to the first Brillouin zone at the expense of the introduction of a new quantum number, the band index n . Since the orbitals φ_ν form a natural basis to represent the field operators $\hat{\psi}_I(\mathbf{r}_1 t_1)$ and $\hat{\psi}_I^\dagger(\mathbf{r}_2 t_2)$, exploiting the mode expansion from Eq.(3.7) and Eq.(3.8) one finds

$$\hat{\psi}_I(\mathbf{r}_1 t_1) = \sum_{\tilde{\mathbf{k}} \leq \mathbf{k}_F} \varphi_{\tilde{\mathbf{k}}\sigma_1}(\mathbf{r}_1 t_1) \hat{c}_{\tilde{\mathbf{k}}\sigma_1} + \sum_{\tilde{\mathbf{k}} > \mathbf{k}_F} \varphi_{\tilde{\mathbf{k}}\sigma_1}(\mathbf{r}_1 t_1) \hat{c}_{\tilde{\mathbf{k}}\sigma_1}^\dagger \quad (3.54)$$

and

$$\hat{\psi}_I^\dagger(\mathbf{r}_2 t_2) = \sum_{\tilde{\mathbf{k}} \leq \mathbf{k}_F} \varphi_{\tilde{\mathbf{k}}\sigma_2}^*(\mathbf{r}_2 t_2) \hat{c}_{\tilde{\mathbf{k}}\sigma_2}^\dagger + \sum_{\tilde{\mathbf{k}} > \mathbf{k}_F} \varphi_{\tilde{\mathbf{k}}\sigma_2}^*(\mathbf{r}_2 t_2) \hat{c}_{\tilde{\mathbf{k}}\sigma_2}. \quad (3.55)$$

The destruction and creation operators c and $c^\dagger$ destroy or create, dependent on the $\tilde{\mathbf{k}}$ -point, a particle or hole respectively. In the context of a filled Fermi sea, a particle can only be created above the Fermi level, while a hole can be created only below the Fermi level, respectively. Hence it is convenient to apply a canonical transformation of the operator $\hat{c}$ into a so called particle

and hole operator denoted by $\hat{a}$ and $\hat{b}$ in the following way:

$$c_{\tilde{\mathbf{k}}\sigma} = \begin{cases} b_{\tilde{\mathbf{k}}\sigma}^\dagger & \text{for } \tilde{\mathbf{k}} < \mathbf{k}_F \\ a_{\tilde{\mathbf{k}}\sigma} & \text{for } \tilde{\mathbf{k}} > \mathbf{k}_F \end{cases} \quad (3.56)$$

$$c_{\tilde{\mathbf{k}}\sigma}^\dagger = \begin{cases} b_{\tilde{\mathbf{k}}\sigma} & \text{for } \tilde{\mathbf{k}} < \mathbf{k}_F \\ a_{\tilde{\mathbf{k}}\sigma}^\dagger & \text{for } \tilde{\mathbf{k}} > \mathbf{k}_F. \end{cases} \quad (3.57)$$

Furthermore, the anticommutation rules between creation and destruction (annihilation) operators due to Eq.(3.12) remain unchanged under this canonical transformation, i.e.

$$\left[\hat{a}_{\tilde{\mathbf{k}}_1, \sigma_1}, \hat{a}_{\tilde{\mathbf{k}}_2, \sigma_2}^\dagger = \hat{b}_{\tilde{\mathbf{k}}_1, \sigma_1}, \hat{b}_{\tilde{\mathbf{k}}_2, \sigma_2}^\dagger = \delta_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2} \delta_{\sigma_1, \sigma_2} \right]_+ . \quad (3.58)$$

As a result, the field operators of Eq.(3.54) and Eq.(3.55) can be recast in the following way

$$\hat{\psi}_I(\mathbf{r}_1 t_1) = \sum_{\tilde{\mathbf{k}} \leq \mathbf{k}_F} \underbrace{\varphi_{\tilde{\mathbf{k}}\sigma_1}(\mathbf{r}_1 t_1) \hat{b}_{\tilde{\mathbf{k}}\sigma_1}^\dagger}_{\hat{\psi}_I^{(+)}(1)} + \sum_{\tilde{\mathbf{k}} > \mathbf{k}_F} \underbrace{\varphi_{\tilde{\mathbf{k}}\sigma_1}(\mathbf{r}_1 t_1) \hat{a}_{\tilde{\mathbf{k}}\sigma_1}}_{\hat{\psi}_I^{(-)}(1)} \quad (3.59)$$

and

$$\hat{\psi}_I^\dagger(\mathbf{r}_2 t_2) = \sum_{\tilde{\mathbf{k}} \leq \mathbf{k}_F} \underbrace{\varphi_{\tilde{\mathbf{k}}\sigma_2}^*(\mathbf{r}_2 t_2) \hat{b}_{\tilde{\mathbf{k}}\sigma_2}}_{\hat{\psi}_I^{(-)\dagger}(2)} + \sum_{\tilde{\mathbf{k}} > \mathbf{k}_F} \underbrace{\varphi_{\tilde{\mathbf{k}}\sigma_2}^*(\mathbf{r}_2 t_2) \hat{a}_{\tilde{\mathbf{k}}\sigma_2}^\dagger}_{\hat{\psi}_I^{(+)\dagger}(2)}. \quad (3.60)$$

The transition into the particle-hole picture and the involved separation of the field operators into creation and destruction operators plays a crucial role in the application of the Wick theorem and also in the subsequent representation of Eq.(3.49) as Feynman diagrams. By virtue of Eq.(3.49), for every order l the series expansion introduces $4 \cdot l + 2$ field operators¹⁵ that need to be reordered following their anticommutation rules. Such tedious task can be simplified with the aid of the Wick theorem. It makes use of the fact that every time ordered product of free field operators can be expressed as a sum of so called *normal ordered* products of field operators plus remaining terms that involve so called contractions. The idea behind this is to reshuffle any product of time ordered free field operators into a sequence whereas all annihilation operators $\hat{\psi}^{(-)}/\hat{\psi}^{(-)\dagger}$ stand to the right of all creation operators $\hat{\psi}^{(+)}/\hat{\psi}^{(+)\dagger}$. The corresponding difference between time ordered and normal ordered products of field operators may be again expressed as a sum of normal ordered products plus terms containing the anticommutator of two field operators. The latter one is however just a simple complex number and is usually denoted as contraction[40]. Since the expectation value of a normal ordered product of free field operators w.r.t. the non-interacting ground state vanishes, i.e.

$$\langle \Phi_0 | \mathcal{N} \hat{A} \hat{B} \dots \hat{Z} | \Phi_0 \rangle = 0, \quad (3.61)$$

¹⁵The interaction term $\hat{V}_{\text{int}}$ in second quantization carries 4 field operators as shown in Eq.(B.1).

the time ordered product can be reduced to the remaining terms of contracted field operators. This is manifested in the Wick theorem:

Wick's theorem. *Any time ordered product of free field operators equals the sum of all normal ordered products containing all possible contractions:*

$$\begin{aligned}
 \mathcal{T} [\hat{A}\hat{B}\hat{C}\dots\hat{Z}] &= \mathcal{N} [\hat{A}\hat{B}\hat{C}\dots\hat{Z}] \\
 &+ \mathcal{N} [\overline{\hat{A}\hat{B}}\hat{C}\dots\hat{Z}] + \dots \\
 &+ \mathcal{N} [\overline{\hat{A}\hat{B}}\overline{\hat{C}\hat{D}}\dots\hat{Z}] + \dots \\
 &+ \dots \\
 &+ \text{all completely contracted pairs.}
 \end{aligned} \tag{3.62}$$

The contraction always comes in pairs of field operators and can be taken out of the expectation value in Eq.(3.62). Evenmore, contractions of field operators become zero if both anticommute. Hence, any possible combinations are restricted to pairs of annihilation and creation operators. In particular, the non-interacting Green's function can be written as the contraction of the free field operators given in the interaction picture [50]

$$G_0(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \frac{1}{i\hbar} \overline{\hat{\psi}_I(\mathbf{r}_1 t_1) \hat{\psi}_I^\dagger(\mathbf{r}_2 t_2)}. \tag{3.63}$$

By separating the field operators into creation and annihilation parts, as shown in Eq.(3.60), the particle and hole character of G_0 can be easily verified. One thus finds

$$i\hbar G_0(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \begin{cases} \hat{\psi}_I^{(-)}(\mathbf{r}_1 t_1) \hat{\psi}_I^{(+)\dagger}(\mathbf{r}_2 t_2) & \text{if } t_1 > t_2 \\ \hat{\psi}_I^{(+)}(\mathbf{r}_1 t_1) \hat{\psi}_I^{(-)\dagger}(\mathbf{r}_2 t_2) & \text{if } t_2 > t_1. \end{cases} \tag{3.64}$$

Within the respective spatial representation, G_0 represents the propagation of a particle added to the non-interacting many-body system in positive time direction, while it yields a hole propagation 'travelling' in negative time direction. One may note that the field operators given within the interaction picture are equivalent to their representation within the Heisenberg picture as both operators are expressed in terms of a non-interacting orbital basis. Eventually, the evaluation of the time ordered product in Eq.(3.49) is equivalent to the summation over all completely contracted pairs of free field operators yielding in total $(4 \cdot l + 2)$ possible combinations of totally contracted field operators for every order l .

Representation by Feynman graphs

Obviously, the pairing of field operators becomes rather confusing the more operators are involved and it becomes impossible to treat all orders of interactions by hand. However, the methods after Feynman to represent the non-interacting Green's function by a single line, indicating the

direction of propagation from the second to the first argument, and the Coulomb interaction given as a wiggly line allows to draw systematically all possible distinct topological Feynman graphs at every order l of interaction. From the perturbation series [Eq.(3.49)] one may verify that the first order term yields

$$\begin{aligned}
 i\hbar G^{(1)}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \left\langle \Phi_0 \left| \left(-\frac{i}{\hbar} \right) \int_{-\infty}^{\infty} dt'_1 \mathcal{T} \left\{ \hat{V}_{\text{int},I}(t'_1) \hat{\psi}_I(1) \hat{\psi}_I^\dagger(2) \right\} \right| \Phi_0 \right\rangle \\
 &= -\frac{i}{\hbar} \left\langle \Phi_0 \left| \frac{1}{2} \sum_{\sigma'_1, \sigma'_2} \int_{-\infty}^{\infty} dt'_1 \int d\mathbf{r}'_1 d\mathbf{r}'_2 \mathcal{T} \left\{ \hat{\psi}_I^\dagger(\mathbf{r}'_1 t'_1) \hat{\psi}_I^\dagger(\mathbf{r}'_2 t'_1) \right. \right. \right. \\
 &\quad \times v(\mathbf{r}'_1, \mathbf{r}'_2; t'_1) \hat{\psi}_I(\mathbf{r}'_2 t'_1) \hat{\psi}_I(\mathbf{r}'_1 t'_1) \hat{\psi}_I(\mathbf{r}_1 t_1) \hat{\psi}_I^\dagger(\mathbf{r}_2 t_2) \left. \left. \right\} \right| \Phi_0 \right\rangle \\
 &\quad \times \frac{1}{\langle \Phi_0 | \hat{S} | \Phi_0 \rangle}.
 \end{aligned} \tag{3.65}$$

The field operators in Eq.(3.65) carry a spin index for each spin orientation as introduced by Eq.(3.54) and Eq.(3.55). Due to the antisymmetrized ground state wave function $|\Phi_0\rangle$ there are 4 different Coulomb interaction terms due to the 2 possible spin orientations for σ'_1 and σ'_2 . Thus, the sum over the spin indices in Eq. (3.65) might be accounted by a factor 4 for non-magnetic systems. Usually, the instantaneous Coulomb interaction term, which is spin independent, is extended in increasing orders to make the integration over spatial and time variables symmetrically. This implies for the rhs of Eq.(3.65) the following expression

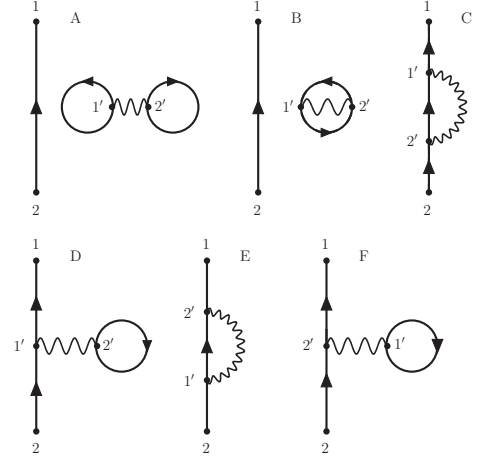
$$\begin{aligned}
 &= -\frac{i}{\hbar} \left\langle \Phi_0 \left| \frac{4}{2} \int_{-\infty}^{\infty} dt'_1 \int_{-\infty}^{\infty} dt'_2 \int d\mathbf{r}'_1 d\mathbf{r}'_2 \mathcal{T} \left\{ \hat{\psi}_I^\dagger(\mathbf{r}'_1 t'_1) \hat{\psi}_I^\dagger(\mathbf{r}'_2 t'_2) \right. \right. \right. \\
 &\quad \times v(\mathbf{r}'_1, \mathbf{r}'_2; t'_1, t'_2) \hat{\psi}_I(\mathbf{r}'_2 t'_2) \hat{\psi}_I(\mathbf{r}'_1 t'_1) \hat{\psi}_I(\mathbf{r}_1 t_1) \hat{\psi}_I^\dagger(\mathbf{r}_2 t_2) \left. \left. \right\} \right| \Phi_0 \right\rangle \\
 &\quad \times \frac{1}{\langle \Phi_0 | \hat{S} | \Phi_0 \rangle},
 \end{aligned} \tag{3.66}$$

where the Coulomb kernel is simply proportional to the delta function, i.e. $v(\mathbf{r}'_1, \mathbf{r}'_2; t'_1, t'_2) = v(\mathbf{r}'_1, \mathbf{r}'_2) \delta(t'_1 - t'_2)$. The application of Wick's theorem results in 6 different terms, each of them contains 3 pairs of contracted field operators or simply 3 products of non-interacting Green's functions. As a result one obtains six distinct Feynman graphs as shown in Fig.(3.2). Obviously, the series expansion yields connected and disconnected Feynman graphs, as well as single lines that are closed. In particular the latter one contradicts the definition of the time ordered Green's function, which has two distinct time arguments. However, such a loop of a fermionic line which is a priori given as $G^{(0)}(\mathbf{r}_1 t_1, \mathbf{r}_1 t_1)$ may be rewritten as

$$G^{(0)}(\mathbf{r}_1 t_1, \mathbf{r}_1 t_1) = \lim_{t_2 \rightarrow t_1^+} G^{(0)}(\mathbf{r}_1 t_1, \mathbf{r}_1 t_2), \tag{3.67}$$

and displays the common applied convention, to follow the normal ordered product that appears in Wick's theorem[50]. Within the space time representation of Feynman diagrams, the vertex

Figure 3.2: Feynman graph representation of the Green's function to first order in the Coulomb interaction. The wiggly line denotes the Coulomb interaction, while the non-interacting Green's function $G_0(1, 2)$ is shown as a solid line with an arrow heading from the second to the first space/time argument, i.e. $1 = \mathbf{r}, t$. Graphs are taken from [50].



• appearing in Fig.(3.2) indicates the spatial variable and a time point on a time axis considered to run from the bottom to the top. The integration in Eq.(3.66) involves only diagrams that are connected by the wiggly Coulomb line and yield complex numbers. Hence, diagrams such as No. A or No. B can be treated as products of complex numbers and may be factored out. Evenmore, the resulting series of disconnected diagrams is exactly canceled by the denominator $\langle \Phi_0 | \hat{S} | \Phi_0 \rangle$, which yields all orders of the vacuum amplitude diagrams[54]. Hence, the perturbation series of the full time ordered Green's function has a Feynman diagram representation including connected diagrams only and the cancellation of the disconnected contributions due to the denominator is known as the *Linked-Cluster theorem*[55]. Therefore, the ultimate perturbation series for the time ordered Green's function can be stated as the following

$$G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \frac{1}{i\hbar} \langle \Phi_0 | \sum_{l=0}^{\infty} \left(-\frac{i}{\hbar} \right)^l \frac{1}{l!} \int_{-\infty}^{\infty} dt'_1 \dots \int_{-\infty}^{\infty} dt'_l \times \mathcal{T} \left\{ \hat{V}_{\text{int},I}(t'_1) \dots \hat{V}_{\text{int},I}(t'_l) \hat{\psi}_I(1) \hat{\psi}_I^\dagger(2) \right\} | \Phi_0 \rangle_{\text{fully connected}}. \quad (3.68)$$

Self-energy insertion

By inspection of Fig.(3.2) one notes that the full interacting Green's function posses a certain characteristic within the Feynman representation. Every diagram has an incoming fermion line propagating the many-body system including the extra particle or hole up to the time point where the interaction begins. The first order approximation clearly gives only one time point at which an interaction can happen, while for every higher order, one further interaction term at another time point is included. After that, the diagram finishes with a further fermion line propagating the many-body system to a second specific time point. The corresponding integral equation may then be written in the following way:

$$G(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = G^{(0)}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) + \int d\mathbf{r}'_1 d\mathbf{r}'_2 \int_{-\infty}^{\infty} dt'_1 dt'_2 G^{(0)}(\mathbf{r}_1 t_1, \mathbf{r}'_1 t'_1) \bar{\Sigma}(\mathbf{r}'_1 t'_1, \mathbf{r}'_2 t'_2) G^{(0)}(\mathbf{r}'_2 t'_2, \mathbf{r}_2 t_2). \quad (3.69)$$

All diagrams, which lie in-between the first and the last fermion line are called self-energy insertions and contain all possible Coulomb interactions to all orders up to infinity. Their contribution summed up to infinity yield the reducible or improper self-energy $\bar{\Sigma}$. However, this quantity can be split up, if one Feynman diagram (at higher orders) contains at least two self-energy insertions connected by a single fermion line. Those diagrams can be cut off at the fermion line and one may write the reducible self-energy itself as an infinite series containing only irreducible or proper self-energy insertions Σ connected by single fermion line. The corresponding integral equation becomes

$$\begin{aligned} \bar{\Sigma}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = & \Sigma(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) + \int d\mathbf{r}'_1 d\mathbf{r}'_2 \int_{-\infty}^{\infty} dt'_1 dt'_2 \\ & \times \Sigma(\mathbf{r}_1 t_1, \mathbf{r}'_1 t'_1) G^{(0)}(\mathbf{r}'_1 t'_1, \mathbf{r}'_2 t'_2) \Sigma(\mathbf{r}'_2 t'_2, \mathbf{r}_2 t_2) + \dots \end{aligned} \quad (3.70)$$

or in shorthand notation

$$\bar{\Sigma} = \Sigma + \Sigma G^{(0)} \Sigma + \Sigma G^{(0)} \Sigma G^{(0)} \Sigma + \dots \quad (3.71)$$

The combination of Eq.(3.69) and Eq.(3.70) result in closed expression for the full time ordered Green's function. In shorthand notation one obtains:

$$\begin{aligned} G &= G^{(0)} + G^{(0)} \bar{\Sigma} G^{(0)} \\ &= G^{(0)} + G^{(0)} \left\{ \Sigma + \Sigma G^{(0)} \Sigma + \Sigma G^{(0)} \Sigma G^{(0)} \Sigma + \dots \right\} G^{(0)} \\ &= G^{(0)} + G^{(0)} \Sigma \left\{ 1 + G^{(0)} \Sigma + G^{(0)} \Sigma G^{(0)} \Sigma + \dots \right\} G^{(0)} \\ &= G^{(0)} + G^{(0)} \Sigma \left\{ G^{(0)} + G^{(0)} \Sigma G^{(0)} + G^{(0)} \Sigma G^{(0)} \Sigma G^{(0)} + \dots \right\} \\ &= G^{(0)} + G^{(0)} \Sigma G. \end{aligned} \quad (3.72)$$

This is just the *Dyson equation* for the time ordered Green's function and is explicitly given as an integral equation

$$\begin{aligned} G(\mathbf{r}_1 t_1, \mathbf{r}'_1 t'_1) &= G^{(0)}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \\ &+ \int d\mathbf{r}'_1 d\mathbf{r}'_2 \int_{-\infty}^{\infty} dt'_1 dt'_2 G^{(0)}(\mathbf{r}_1 t_1, \mathbf{r}'_1 t'_1) \Sigma(\mathbf{r}'_1 t'_1, \mathbf{r}'_2 t'_2) G(\mathbf{r}'_2 t'_2, \mathbf{r}_2 t_2). \end{aligned} \quad (3.73)$$

One may note that Eq.(3.73) is equivalent to Eq.(3.40) within the zero temperatur limit.¹⁶

3.4.3. Single particle excitations and quasiparticles

The coming section is devoted to the calculation of the excitation energies of a many-body system in the context of the quasiparticle picture. As it has been discussed in section 3.2, quasiparticle

¹⁶The Dyson equation given by Eq.(3.73) differs from Eq.(3.40) only by the fact that the non-interacting Green's function obeys the equation of motion [see Eq.(3.39)] excluding the classical Hartree term and excluding a mean-field approximation of the exchange and correlation effects mediated by a corresponding potential V_{xc} .

energies can be identified as the corresponding energy levels of a many-body system and need to have life times that are reasonably long to be accessible by an experimental measurement. The condition of infinite life times would be trivially fulfilled in the case of independent particles. In this case, the corresponding Green's function $G^{(0)}$ is readily accessible and yields, assuming the mode expansion of Eq.(3.59) and Eq.(3.60), the following expression[44]

$$G^{(0)}(\mathbf{r}_1, \mathbf{r}_2; z) = \sum_{\tilde{\mathbf{k}}} \frac{\varphi_{\tilde{\mathbf{k}}}(\mathbf{r}_1) \varphi_{\tilde{\mathbf{k}}}^*(\mathbf{r}_2)}{\hbar z - \varepsilon_{\tilde{\mathbf{k}}}}. \quad (3.74)$$

Assuming a reference system of independent particles that already include a certain amount of exchange and correlation effects due to a mean-field approach, the solution of the equation of motion for $G^{(0)}$ [compare Eq.(3.39)] in the frequency domain, requires the solution of the one-particle Schrödinger equation

$$\left[-\frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 + V_{\text{ion}}(\mathbf{r}_1) + V_{\text{H}}(\mathbf{r}_1) \right] \varphi_{\tilde{\mathbf{k}}}(\mathbf{r}_1) + \int d\mathbf{r}'_1 V_{\text{xc}}(\mathbf{r}_1, \mathbf{r}'_1) \varphi_{\tilde{\mathbf{k}}}(\mathbf{r}'_1) = \varepsilon_{\tilde{\mathbf{k}}} \varphi_{\tilde{\mathbf{k}}}(\mathbf{r}_1). \quad (3.75)$$

Since the eigenvalues $\varepsilon_{\tilde{\mathbf{k}}}$ equally represents the excitation energies of the non-interacting many-body system, the corresponding spectral function has distinct delta peaks at those eigenvalues. Considering the definition of the spectral function, given by Eq.(3.25), one may find with Eq.(E.3) and Eq.(E.4)

$$A(\mathbf{r}_1, \mathbf{r}_2; \omega) = 2\pi \sum_{\tilde{\mathbf{k}}} \varphi_{\tilde{\mathbf{k}}}(\mathbf{r}_1) \varphi_{\tilde{\mathbf{k}}}^*(\mathbf{r}_2) \delta(\hbar\omega - \varepsilon_{\tilde{\mathbf{k}}}). \quad (3.76)$$

Since the density of states $D(\hbar\omega)$ is just given by $\sum_{\tilde{\mathbf{k}}} \delta(\hbar\omega - \varepsilon_{\tilde{\mathbf{k}}})$, one finds the following relation to the spectral function in the independent particle case

$$2\pi D(\hbar\omega) = \text{tr} A(\omega) = \sum_{\tilde{\mathbf{k}}} A_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}(\omega). \quad (3.77)$$

The situation is more complicated in the case of interacting particles and the question of an equivalent representation of the Green's function and its corresponding spectral function needs to be answered. Considering the equation of motion for G [Eq.(3.37)], the operator equation in the frequency domain leads to a formal solution (resolvent of G)[56, 48]

$$G(\mathbf{r}_1, \mathbf{r}_2; z) = \sum_{\tilde{\mathbf{k}}} \frac{\phi_{\tilde{\mathbf{k}}}(\mathbf{r}_1; z) \bar{\phi}_{\tilde{\mathbf{k}}}^*(\mathbf{r}_2; z)}{\hbar z - E_{\tilde{\mathbf{k}}}(z)}, \quad (3.78)$$

whereas the set of eigenfunctions $\{\phi_{\tilde{\mathbf{k}}}(z)\}$ and $\{\bar{\phi}_{\tilde{\mathbf{k}}}(z)\}$ form a bi-orthogonal system, obeying the eigenvalue problem

$$\left[-\frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 + V_{\text{ion}}(\mathbf{r}_1) + V_{\text{H}}(\mathbf{r}_1) \right] \phi_{\tilde{\mathbf{k}}}(\mathbf{r}_1; z) + \int d\mathbf{r}'_1 \Sigma^{\text{xc}}(\mathbf{r}_1, \mathbf{r}'_1; z) \phi_{\tilde{\mathbf{k}}}(\mathbf{r}'_1; z) = E_{\tilde{\mathbf{k}}}(z) \phi_{\tilde{\mathbf{k}}}(\mathbf{r}_1; z) \quad (3.79)$$

¹⁷For the zero-temperature limit, $G^{(0)}$ has only a real frequency argument and the substitution $\hbar z \rightarrow \hbar\omega + i\text{sgn}(\hbar\omega - \mu)\eta$ has to be taken into account.

that needs to be solved for every frequency z . Since the self-energy operator is non-hermitian the resulting eigenvalues will in general be complex numbers.

Quasiparticle approximation

As it is obvious from Eq.(3.78) one may expect $G(z)$ to have poles where the complex energy $E_{\tilde{\mathbf{k}}}(z) = \hbar z$. Separating into real and imaginary part, i.e. $E_{\tilde{\mathbf{k}}}(z) = \Re E_{\tilde{\mathbf{k}}}(z) + i\Im E_{\tilde{\mathbf{k}}}(z)$ one may assume that the spectral function has a dominant peak at $\Re E_{\tilde{\mathbf{k}}}(z)$. Keeping that in mind, one finds initially for the spectral function the following expression[44, 57]

$$A_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}(\omega) = \frac{2|\Im \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(\omega)|}{\left[\hbar\omega - \varepsilon_{\tilde{\mathbf{k}}} - \Re \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(\omega)\right]^2 + \left[\Im \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(\omega)\right]^2}. \quad (3.80)$$

If the imaginary part $\Im \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(\omega)$ at the frequency ω is much smaller than the remaining part in the denominator, the matrix element of the spectral function will in general have a dominant peak at the quasiparticle energy defined as

$$E_{\tilde{\mathbf{k}}}^{\text{qp}} = \varepsilon_{\tilde{\mathbf{k}}} + \Re \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}\left(E_{\tilde{\mathbf{k}}}^{\text{qp}}/\hbar\right). \quad (3.81)$$

Under the assumption of a slowly varying imaginary part of the self-energy in Eq.(3.80) one may expand the spectral function around the quasiparticle energy in a Taylor series up to first order and obtains a corresponding quasiparticle approximation of the latter one [48]

$$A_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}(\omega) \approx Z_{\tilde{\mathbf{k}}} \frac{2Z_{\tilde{\mathbf{k}}} \left| \Im \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(E_{\tilde{\mathbf{k}}}^{\text{qp}}/\hbar) \right|}{\left(\hbar\omega - E_{\tilde{\mathbf{k}}}^{\text{qp}}\right)^2 + \left[Z_{\tilde{\mathbf{k}}} \Im \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}\left(E_{\tilde{\mathbf{k}}}^{\text{qp}}/\hbar\right)\right]^2}. \quad (3.82)$$

Hence, the quasiparticle approximation leads to a Lorentzian form of the spectral function at the corresponding excitation energy with a width at half maximum $\Gamma = Z_{\tilde{\mathbf{k}}} \Im \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(E_{\tilde{\mathbf{k}}}^{\text{qp}}/\hbar)$. The spectral weight is then determined by the renormalization factor

$$Z_{\tilde{\mathbf{k}}} = \left(1 - \frac{\partial \Re \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(\omega)}{\partial(\hbar\omega)} \bigg|_{\hbar\omega=E_{\tilde{\mathbf{k}}}^{\text{qp}}}\right)^{-1} \quad (3.83)$$

and equals the residuum of the Green's function [Eq.(3.78)] at the quasiparticle energy [56]. With the definition for the quasiparticle energy and the corresponding qp-approximation for the spectral function, the Green's function can be written as

$$G^{\text{qp}}(\mathbf{r}_1, \mathbf{r}_2; z) = \sum_{\tilde{\mathbf{k}}} Z_{\tilde{\mathbf{k}}} \frac{\phi_{\tilde{\mathbf{k}}}(\mathbf{r}_1) \bar{\phi}_{\tilde{\mathbf{k}}}^*(\mathbf{r}_2)}{\hbar z - \left[E_{\tilde{\mathbf{k}}}^{\text{qp}}(z) + iZ_{\tilde{\mathbf{k}}} \Im \Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(E_{\tilde{\mathbf{k}}}^{\text{qp}}/\hbar)\right]}. \quad (3.84)$$

The expression above allows for the interpretation of a decaying particle with a life time $\tau = \hbar/\Gamma$ [30]. The finite life time is associated with the correlation effects, i.e. the interaction among the quasiparticles. One drawback of the quasiparticle approximation is the violation of the sum rule

of the spectral function. However, in order to discuss quasiparticle excitations, one usually sets the renormalization factor to 1 and hence associates the full spectral weight to the dominant peak in the spectral function. Furthermore, it is convenient to neglect the imaginary part of the self energy $\Im\Sigma^{\text{xc}}$. Hence the resulting quasiparticle has an infinite life time and can, under these circumstances, be treated as an ideal quasi particle. Additionally, the eigenvalue problem in Eq.(3.79) becomes a hermitian EVP with real eigenvalues, the quasiparticle energies, and corresponding quasi particle eigenfunctions $\phi_{\mathbf{k}}^{\text{qp}}$. Its evaluation at the quasiparticle energy yields the corresponding quasiparticle equation

$$\left[-\frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 + V_{\text{ion}}(\mathbf{r}_1) + V_{\text{H}}(\mathbf{r}_1) \right] \phi_{\mathbf{k}}^{\text{qp}}(\mathbf{r}_1) + \int d\mathbf{r}'_1 \Sigma^{\text{xc}}(\mathbf{r}_1, \mathbf{r}'_1; E_{\mathbf{k}}^{\text{qp}}/\hbar) \phi_{\mathbf{k}}^{\text{qp}}(\mathbf{r}'_1) = E_{\mathbf{k}}^{\text{qp}} \phi_{\mathbf{k}}^{\text{qp}}(\mathbf{r}_1). \quad (3.85)$$

This simplification to ideal quasiparticles is a priori not justified, however, for weakly correlated systems the renormalization factor is in the range of 0.6 – 0.9 and ensures an appropriate quasiparticle description [58, 59]. Lastly, the quasiparticle wave functions are still unknown, but they can be expanded in terms of the orbitals of the chosen reference system as the following

$$\phi_{\mathbf{k}}^{\text{qp}}(\mathbf{r}_1) = \sum_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}'} c_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}'} \varphi_{\tilde{\mathbf{k}}'}(\mathbf{r}_1). \quad (3.86)$$

Usually, one approximates the qp wave functions simply by the orbitals of the reference systems, i.e. $\phi_{\mathbf{k}}^{\text{qp}}(\mathbf{r}_1) \approx \varphi_{\tilde{\mathbf{k}}}(\mathbf{r}_1)$, which in the case of semiconductors yields reasonable results [58]. Hence, the quasiparticle Green's function is then given by

$$G^{\text{qp}}(\mathbf{r}_1, \mathbf{r}_2; z) = \sum_{\tilde{\mathbf{k}}} \frac{\varphi_{\tilde{\mathbf{k}}}(\mathbf{r}_1) \varphi_{\tilde{\mathbf{k}}}^*(\mathbf{r}_2)}{\hbar z - E_{\tilde{\mathbf{k}}}^{\text{qp}}(z)}. \quad (3.87)$$

Some remarks are necessary at this point. The expression of the spectral function in the basis of the reference system goes back to the corresponding expansion of the Green's function in this particular basis, aiming to obtain an approximative expression for the corresponding expansion coefficient $G_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}'}$. By doing so, the Dyson equation in frequency space may be written as

$$G_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}'}(z) = G_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{(0)}(z) \left[\delta_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}'} + \sum_{\tilde{\mathbf{k}}''} \delta\Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}''}^{\text{xc}}(z) G_{\tilde{\mathbf{k}}''\tilde{\mathbf{k}}}^{\tilde{\mathbf{k}}}(z) \right] \quad \text{with} \quad \delta\Sigma^{\text{xc}} = \Sigma^{\text{xc}} - V_{\text{xc}} \quad (3.88)$$

and yields a coupled system of equation that decouples only if the condition $\delta\Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}''}^{\text{xc}} \ll \varepsilon_{\tilde{\mathbf{k}}} - \varepsilon_{\tilde{\mathbf{k}}'}$ is fulfilled [44]. If so, the resulting Green's function is diagonal w.r.t. the reference basis, i.e.

$$G_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}(z) = G_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{(0)}(z) \left[1 + \delta\Sigma_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\text{xc}}(z) G_{\tilde{\mathbf{k}}\tilde{\mathbf{k}}}^{\tilde{\mathbf{k}}}(z) \right], \quad (3.89)$$

and eventually leads to the matrix elements of the spectral function [Eq.(3.80)], if the definition of $A(\omega)$ [Eq.(E.19)] is exploited. Additionally, the quasiparticle picture is just a model-picture

and has little to do with the exact Green's function which has poles only at the real frequency axis which are associated with sharp delta peaks in the corresponding spectral function (infinite life times).

3.5. Hedin's set of equations

In principle the full time ordered Green's function has a unique series expansion in terms of the Coulomb interaction and thus allows for a systematic expansion. The question arising immediately is which kind of subseries within the full expansion are to be chosen to give a convergent result. As Hedin pointed out in his seminal publication [4] it is convenient to have a series expansion in terms of a screened Coulomb interaction that already accounts for effects of polarization and hence yields an improved convergence rate. In this context, polarization effects emerge simply due to the repelling effect between electrons. As charges are shifted 'away' from each other, a positive net charge accumulates in the vicinity around a picked electron and thus polarizes the medium and reduces or screen the interaction with the remaining electrons.

3.5.1. Variational method

The aim of the variational method is to give an explicit expression for the two-particle Green's function that emerges in the derivation of the equation of motion for the causal Green's G . One makes use of the Schwinger functional derivative technique which allows to investigate the Coulomb interaction of the injected particle or hole in the presence of an external potential [46]. The underlying Hamiltonian consists of the many-particle Hamiltonian Eq.(2.1) plus a perturbation term $\hat{H}'_{\text{ext}}$ due to an external potential $\mathcal{U}(\mathbf{r})$

$$\hat{H}'_{\text{ext}}(t) = \int d\mathbf{r} \hat{\psi}^\dagger(\mathbf{r}, t) \mathcal{U}(\mathbf{r}) \hat{\psi}(\mathbf{r}, t). \quad (3.90)$$

The time dependence is mediated by the field operators given in the Heisenberg picture. In general the external potential may also explicitly depend on time, while a time independent potential allows to identify the external potential by a real physical potential such as an external test charge. Due to the two contributions to the current Hamiltonian, i.e. $\hat{H} = \hat{H}_0 + \hat{H}'_{\text{ext}}(t)$,¹⁸ the underlying time evolution operator (within the Schrödinger picture) reads

$$\hat{U}(t) = e^{-\frac{i}{\hbar}(\hat{H}_0 + \hat{H}'_{\text{ext}})t}. \quad (3.91)$$

With regard to the separation of $\hat{H}$ into an unperturbed and perturbed part, the time evolution operator [Eq.(3.91)] can be decomposed into the product

$$\hat{U}(t) = e^{-\frac{i}{\hbar}\hat{H}_0 t} \mathcal{S}(t, t_0) \quad (3.92)$$

where $\mathcal{S}$ is denoted as the scattering matrix. It is equivalent to the time evolution operator in the interaction picture [compare Eq.(D.7)]. As a result, one may define a new Green's function

¹⁸We treat $\hat{H}_0$ as the many-body Hamiltonian given by Eq.(2.1).

as a functional of $\mathcal{U}$ in analogy with the series expansion shown in section 3.4.2, whereas the interacting term, previously the Coulomb interaction [see Eq.(3.49)], is now governed by the external potential within the interaction picture $\hat{H}'_{\text{ext},I}(t)$. With respect to the series representation of the time evolution operator in the interaction picture the Green's function may be written as [60]

$$i\hbar G(1, 2; \mathcal{U}) = {}_{\mathcal{U}} \left\langle \Psi_0 \left| \mathcal{T} \hat{\psi}_{\mathcal{U}}(1) \hat{\psi}_{\mathcal{U}}^\dagger(2) \right| \Psi_0 \right\rangle_{\mathcal{U}} = \frac{\left\langle \Psi_0 \left| \mathcal{T} \mathcal{S} \hat{\psi}_{\mathcal{U},I}(1) \hat{\psi}_{\mathcal{U},I}^\dagger(2) \right| \Psi_0 \right\rangle}{\left\langle \Psi_0 \left| \mathcal{S} \right| \Psi_0 \right\rangle}. \quad (3.93)$$

The subscript ${}_{\mathcal{U}} \langle \dots \rangle_{\mathcal{U}}$ denotes the perturbed many-particle state due to the external potential. Additionally, the field operators $\hat{\psi}_{\mathcal{U}}$ denote their representation within the Heisenberg picture w.r.t the Hamiltonian $\hat{H}_0 + \hat{H}'_{\text{ext}}$ and $\hat{\psi}_{\mathcal{U},I}$ are the field operators within the according interaction picture. On the other hand, the representation including the scattering matrix on the right hand side, describes the propagation of the initially (at $t_0 = -\infty$) unperturbed ground state within the time intervall $[t_2, -\infty]$, the propagation of the injected particle from the time points $t_2 \rightarrow t_1$ and finally the propagation of $|\Psi_0\rangle$ in the intervall $[\infty, t_1]$. During this process, $\mathcal{U}$ is assumed to vanish at infinity. Since the external potential is treated as a small perturbation, the Green's function can be linearized and yield the desired relation to the two-particle Green's function[46, 60]

$$\frac{\delta G(12; \mathcal{U})}{\delta \mathcal{U}(3^+)} = G(12; \mathcal{U}) G(33^+; \mathcal{U}) - G(1, 3, 2, 3^+; \mathcal{U}). \quad (3.94)$$

In analogy with the definition of the self-energy Σ [Eq.(3.36)], the two particle Green's function in Eq.(3.94) can be used to define the corresponding self-energy as a functional of the external potential, i.e. $\Sigma(\mathcal{U})$ with

$$\Sigma(12; \mathcal{U}) = -i\hbar \int d3 d4 v(1-3) G(1, 3, 4, 3^+; \mathcal{U}) G^{-1}(42; \mathcal{U}). \quad (3.95)$$

The comparison of Eq.(3.95) with Eq.(3.94) immediately reveals the separation of the self-energy $\Sigma(\mathcal{U})$ into the classical Hartree term $\Sigma_H(\mathcal{U})$ ¹⁹ and the remaining term $\Sigma^{\text{xc}}(\mathcal{U})$ that includes all exchange and correlation effects. This might be shown by plugging the expression for the two-particle Green's function due to Eq.(3.94) into Eq.(3.95). One thus obtains

$$\Sigma(12; \mathcal{U}) = -i\hbar \delta(1-2) \int d3 v(1-3) G(33^+) + i\hbar \int d3 d4 \frac{\delta G(14; \mathcal{U})}{\delta \mathcal{U}(3^+)} G^{-1}(42; \mathcal{U}). \quad (3.96)$$

Thereby, the definition of the inverse Green's function due to Eq.(3.34) has been used to obtain the Hartree term Σ_H (first term of Eq.(3.96)). Moreover, from the identity due to Eq.(3.34), one deduces the relation

$$\int d2 \frac{\delta G(12; \mathcal{U})}{\delta \mathcal{U}(3^+)} G^{-1}(24; \mathcal{U}) = - \int d2 G^{-1}(12; \mathcal{U}) \frac{\delta G(24; \mathcal{U})}{\delta \mathcal{U}(3^+)}. \quad (3.97)$$

¹⁹Compare with Eq.(3.38).

that is beneficial to rewrite the exchange-correlation term Σ^{xc} (the second term of Eq.(3.96)) in the following way:

$$\Sigma^{\text{xc}}(12;U) = -i\hbar \int d3 d4 G(14;U) \frac{\delta G^{-1}(42;U)}{\delta U(3^+)}. \quad (3.98)$$

Hence, the introduction of a small external potential provides a useful tool to determine the full self-energy simply by the functional derivative $\frac{\delta G}{\delta U}$. Nevertheless, the external potential is an arbitrary quantity and the formalism of the variational method shall be valid for any U . In particular, in the limes of a vanishing external potential, one imposes the condition $\lim_{U \rightarrow 0} \Sigma(U) = \Sigma$.

3.5.2. Microscopic response functions

Through the action of a small external perturbation, we may also derive microscopic response quantities such as the dielectric function that relates the external potential to the effective potential. The latter one is just given by the sum of the external potential plus the induced potential. This can also be verified if one considers the equation of motion for $G(U)$ and introduces the effective potential U_{eff} as an auxiliary quantity:

$$\left\{ i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 - V_{\text{ion}}(\mathbf{r}_1) - V_{\text{H}}(\mathbf{r}_1) - U_{\text{eff}}(1) \right\} G(12;U) - \int d3 \Sigma^{\text{xc}}(13;U) G(32;U) = \delta(1-2) \quad (3.99)$$

with

$$U_{\text{eff}}(1) = U(1) - i\hbar \int d2 v(1-2) \{ G(22^+;U) - G(22^+) \} \quad (3.100)$$

and

$$V_{\text{H}}(\mathbf{r}_1) = -i\hbar \int d2 v(1-2) G(2, 2^+). \quad (3.101)$$

Since the Green's function $G(11^+)$ yields the density, the difference in the curly brackets can be identified with the induced density due to the external potential. Again, we regard the external potential as small perturbation and find the response of the considered system with the inverse longitudinal dielectric function given by

$$\epsilon^{-1}(12) = \left. \frac{\delta U_{\text{eff}}(1)}{\delta U(2)} \right|_{U=0}. \quad (3.102)$$

The initially desired expansion of the self-energy in terms of a screened Coulomb potential can now also be established. If we take the exchange and correlation part, i.e. Eq.(3.98) into account, the chain rule of functional derivatives allows to rewrite $\Sigma^{\text{xc}}(U)$ in the following way

$$\Sigma^{\text{xc}}(12;U) = -i\hbar \int d3 d4 d5 v(1-3) G(14;U) \frac{\delta G^{-1}(42;U)}{\delta U_{\text{eff}}(5)} \frac{\delta U_{\text{eff}}(5)}{\delta U(3^+)}. \quad (3.103)$$

Since the last term of the rhs in Eq.(3.103) is the inverse dielectric function, it hence modifies the Coulomb potential as it describes the screening effects of the electronic system. This suggests to

introduce the screened potential W through the definition

$$W(12) = \int d3 v(1-3)\epsilon^{-1}(23). \quad (3.104)$$

Additionally, the explicit evaluation of ϵ^{-1} [Eq.(3.102)] leads to the *polarization function* P

$$P(12) = -i\hbar \frac{\delta G(11^+; \mathcal{U})}{\delta \mathcal{U}_{\text{eff}}(2)} \Big|_{\mathcal{U}=0} \quad (3.105)$$

and the introduction of the vertex function Γ in Eq.(3.103) defined as

$$\Gamma(12; 3) = \frac{\delta G^{-1}(12; \mathcal{U})}{\delta \mathcal{U}_{\text{eff}}(3)} \Big|_{\mathcal{U}=0} \quad (3.106)$$

leads to a closed set of equation once introduced by Hedin [4, 30]. By the explicit calculation of the functional derivatives one obtains the set of integro-differential equations

$$\Sigma^{\text{xc}}(12) = -i\hbar \int d3 d4 G(13)W(14^+)\Gamma(32; 4) \quad (3.107)$$

$$W(12) = v(1-2) + \int d3 d4 W(13)P(34)v(2-4) \quad (3.108)$$

$$P(12) = - \int d3 d4 P_0(1, 1^+, 4, 3)\Gamma(34; 2) \quad (3.109)$$

$$\Gamma(12; 3) = -\delta(1-2)\delta(1-3) + \int d4 d5 d6 d7 \Xi(2, 1, 4, 5)P_0(4, 5, 7, 6)\Gamma(67; 3). \quad (3.110)$$

$$G(12) = G^{(0)}(12) + \int d3 d4 G^{(0)}(13)\Sigma^{\text{xc}}(34)G(42) \quad (3.111)$$

that completely describe the many-particle interactions. Additionally, for simplification, we have introduced the polarization function of independent particles denoted by P_0 . It is given as the product of two Green's function and reads

$$P_0(1, 2, 3, 4) = -i\hbar G(14)G(32). \quad (3.112)$$

By virtue of Eq.(3.110) and Eq.(3.109) one verifies that the three-point vertex function $\Gamma(12; 3)$ generates an integral equation for $P(12)$ that allows to extend the polarization function to a three-point function, i.e. $P(1, 3, 2, 2^+)$. The three-point expression origins from the extended definition of the polarization function

$$P(12) = P(1, 1^+, 2, 2^+). \quad (3.113)$$

Eventually, an integral equation for $P(1, 3, 2, 2^+)$ might be written within a generalized four-point notation giving rise to the so-called *Bethe-Salpeter equation* of the polarization function²⁰ in the following form

$$P(1, 3, 2, 4) = P_0(1, 3, 2, 4) + \int d5 d6 d7 d8 P_0(1, 3, 6, 5) \Xi(6, 5, 7, 8) P(7, 8, 2, 4), \quad (3.114)$$

where the integral kernel, which is given by

$$\Xi(1, 2, 3, 4) = -\frac{1}{i\hbar} \frac{\delta \Sigma^{\text{xc}}(21)}{\delta G(34)}, \quad (3.115)$$

mediates the electron-hole interaction. A derivation of Eq.(3.114) is presented in appendix F. In the context of the Feynman graphs, the polarization function P is equivalent with the representation of the irreducible polarization diagrams, which will be discussed later on.

3.5.3. Density correlation function and microscopic dielectric function

Within the context of the functional derivatives w.r.t an external potential, we want to derive a further important quantity, the density correlation function. This quantity can also be derived from the Kubo formalism [61] as the response quantity that yields the induced density or density variation due to an external perturbation and hence allows to calculate the dielectric properties via the dielectric function ϵ . If one carries out the derivative in Eq.(3.102) one initially finds

$$\epsilon(12)^{-1} = \delta(1 - 2) + \int d3 v(1 - 3) L(32), \quad (3.116)$$

where the *density correlation function* L is given by

$$L(12) = -i\hbar \left. \frac{\delta G(11^+; \mathcal{U})}{\delta \mathcal{U}(2)} \right|_{\mathcal{U}=0}. \quad (3.117)$$

The comparison with Eq.(3.94) and the definition of the two-particle Green's function [Eq.(3.33)] indeed reveals that L is equivalent to the causal density variation operator $\Delta\hat{\rho}$:

$$L(12) = \frac{1}{i\hbar} \langle \mathcal{T} \Delta\hat{\rho}(1) \Delta\hat{\rho}(2) \rangle \quad \text{and} \quad \Delta\hat{\rho}(1) = \hat{\rho}(1) - \langle \hat{\rho}(1) \rangle \quad \rho(1) = \psi^\dagger(1)\psi(1). \quad (3.118)$$

In other words, the density correlation function describes the time-ordered propagation of a density variation between the space-time point $\mathbf{r}_2 t_2 \rightarrow \mathbf{r}_1 t_1$, caused by the action of an external potential at $\mathbf{r}_2 t_2$. With the aid of the chain rule of functional derivatives [appendix A], the rhs of Eq.(3.117) may be rewritten in the following way

$$L(12) = \int d3 P(13) \epsilon^{-1}(32) \quad (3.119)$$

²⁰The extension to the four point quantity $P(1, 3, 2, 4)$ is obtained if one considers the transition $1^+ \rightarrow 3$ and $2^+ \rightarrow 4$.

which allows, using Eq.(3.116), to formulate a Dyson equation for the density correlation function

$$L(12) = P(12) + \int d3 d4 P(13)v(3-4)L(42). \quad (3.120)$$

Finally, the approach to the dielectric function follows from the integral equation in Eq.(3.119) if we use the inverse identity for the dielectric function, i.e.

$$\int d3 \epsilon^{-1}(1,3)\epsilon(3,1). \quad (3.121)$$

The polarization function P might be linked to the density correlation function L as the following

$$P(12) = \int d3 L(13) \epsilon(32). \quad (3.122)$$

Due to the Dyson equation [Eq.(3.120)] one thus finds the integral equation for the dielectric function

$$\epsilon(12) = \delta(1-2) - \int d3 v(1-3)P(32). \quad (3.123)$$

If one considers the definitions for the polarization function P and the density correlation function L , one recognizes that P cannot be treated as a response quantity due to an external perturbation, as it determines the response of the system due to a variation of the effective field. Thus, one has to solve the problem for the inverse dielectric function [Eq.(3.116)] first, in order to obtain the dielectric properties. The extension of the density correlation function $L(12)$ to a general four-point quantity $L(1, 1^+, 2, 2^+)$ can also be performed in the expression of the Dyson equation [Eq.(3.120)]. This, however, does not yield a closed integral equation such as the Bethe-Salpeter equation for P [Eq.(3.114)] in the limit $1^+ \rightarrow 3$ and $2^+ \rightarrow 4$. Nevertheless, as shown in the appendix G, an integral equation similar to Eq.(3.114) can be obtained for the density correlation function L as well:

$$L(1, 3, 2, 4) = L_0(1, 3, 2, 4) + \int d5 d6 d7 d8 L_0(1, 3, 6, 5) \Xi'(6, 5, 7, 8) L(7, 8, 2, 4) \quad (3.124)$$

The kernel now contains the full self-energy Σ including the Hartree term Σ_H and reads

$$\Xi'(1, 2, 3, 4) = -\frac{1}{i\hbar} \frac{\delta \Sigma(21; \mathcal{U})}{\delta G(34; \mathcal{U})} \Big|_{\mathcal{U}=0}. \quad (3.125)$$

Furthermore, L_0 is identical to the polarization function P_0 from Eq.(3.112), i.e. $L_0 = P_0$. As an side effect, the four-point extension of the density correlation function, allows to relate it to the two-particle Green's function in the following way:

$$L(1, 3, 2, 4) = i\hbar \{G(1, 2, 3, 4) - G(13)G(24)\}.^{21} \quad (3.126)$$

²¹One note the different sequence of arguments in $L(1, 3, 2, 4)$ compared to $G(1, 2, 3, 4)$, which retains the two point density correlations function $L(12) = L(1, 1^+, 2, 2^+)$ in the limiting case $3 \rightarrow 1^+$ and $4 \rightarrow 2^+$.

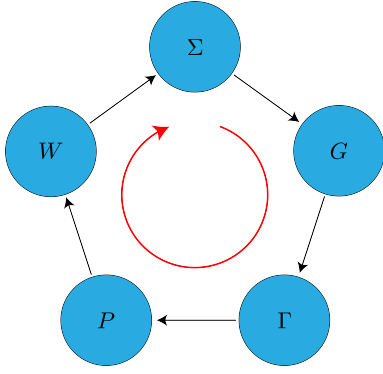


Figure 3.3: Iteration cycle to solve Hedin's equations. To initiate the cycle the self energy is set to zero, i.e. $\Sigma = 0$ with the result of the *GW*-approximation for the self-energy after the first iteration.

The equation above is usually referred to, if the density correlation function is derived from a Feynman graph analysis [see also chapter 7].

3.6. *GW*-approximation

The solution of Hedin's equation together with the Dyson equation is a rather complicated task, because the self-energy itself is a functional of the Green's function, while the latter one should coincide with Eq.(3.107) and Eq.(3.111) at the same footing. Hence, to obtain a self-consistent solution to this problem, it is convenient to start with an initial approximation for the self-energy, which decouples the functional dependence of Σ^{xc} w.r.t G . This immediately leads to the starting point

$$\Sigma^{\text{xc}}(12) = 0 \quad (3.127)$$

and subsequently to an iteration of Hedin's equation as shown in Fig.(3.3). If one follows this iteration cycle, the Green's function is given by the non-interacting Green's function within the Hartree-approximation, while the vertex function becomes

$$\Gamma(12, 3) = -\delta(1-2)\delta(1-3). \quad (3.128)$$

Thus, in the first iteration cycle, vertex corrections due to electron-hole interactions are completely neglected and means that the polarization function is to be replaced by the random phase approximation

$$P(12) = P_0(1, 1^+, 2, 2^+) = -i\hbar G_0(12)G_0(21). \quad (3.129)$$

This in turn generates a self-consistent integral equation for the screened Coulomb interaction in the following way

$$W(12) = v(1-2) + \int d3 d4 W(14)P_0(34)v(2-4) \quad (3.130)$$

and finally yields the *GW*-approximation of the self-energy

$$\Sigma^{\text{xc}}(12) = i\hbar G(12)W(1^+2). \quad (3.131)$$

Basically, the iteration cycle can be performed until a self-consistent result is obtained for the Green's function. However, even at the second iteration step the evaluation of Ξ [Eq.(3.115)] is required to update the vertex function Γ [Eq.(3.110)]. The latter one, however, is given only implicitly and gives no explicit solution for vertex function [30]. To circumvent this problem, Hedin suggested to stick to a power expansion of Σ^{xc} and the polarization function P in terms of the screened potential only [30]. For systems with a large polarizability, such as valence electrons in metals and semiconductors that have a strong screening, one expects to obtain a fast convergence of the expansion of Σ^{xc} w.r.t the screened interaction. In fact, the *GWA* can be seen as an extension to the early developed Hartree-Fock approximation, with the substitution of the bare Coulomb potential with the screened interaction. Hence, correlation effects are included within the dynamical interaction W and give rise to an improved description of quasiparticle energies and corresponding life times [62]. If one considers only the static contributions of W , one obtains the so-called *COHSEX* (Coulomb hole plus screened exchange) approximation [4]. This corresponds, as the name suggests, to a separation of Σ^{xc} into a screened exchange part, plus a Coulomb hole term that describes the interaction of the added particle via an induced (local) potential with the surrounding electrons [63, 58]. An early approximate version of the *GW*-approximation has been already developed before Hedin came up with his equations, and is known as the *shielded potential approximation* [64]. Concerning the full self-consistent iteration of Hedin's equation, a possible disentanglement of Eq.(3.110) w.r.t the vertex function has been shown in [65] and gives a recipe to systematically include vertex correction that go beyond the *GW*-approximation.

Practical application and quasiparticle energies

Since the iteration of Hedin's equation after the first cycle is already a rather involved task, one usually sticks to the neglect of vertex corrections and tries to find the most sophisticated *GW*-approximation. This basically involves the question which orbital basis set is to be chosen for the Green's function and hence for the calculation of the screened interaction. If one considers Hedin's equation alone, the Green's function is given within the Hartree approximation. This however, is not an appropriate starting point, since neither the resulting orbital energies nor the orbitals are reasonable quantities to describe a many-particle system²². Evenmore, the resulting density cannot be compared to the true ground state density, as it is the case within density functional theory. Therefore, the Kohn-Sham formalism seems to serve as a well defined starting point, as it guarantees an appropriate approximation of the ground state density. By doing so, the self-energy is now initially approximated by the corresponding exchange-correlation potential, i.e. $\Sigma^{\text{xc}} = V_{\text{xc}}$. The resulting Green's function G_0 is thus constructed from the orbitals and eigenvalues of the corresponding eigenvalue problem [Eq.(2.26)]. Due to the non-vanishing self-energy, the vertex function [Eq.(3.110)] yields contributions that go beyond the bare vertex [Eq.(3.128)] and enters into the calculation of the polarization function and hence into the screened interaction [66, 58, 62, 67]. If these vertex corrections are taken into account

²²The Hartree approximation neglects completely effects of the antisymmetric interactions (exchange term) and includes self-interaction effects.

one obtains the so-called *GWT*-approximation for the self-energy, and the screened interaction is then given beyond the RPA approximation. In practical calculations, however, these vertex corrections are not taken into account, and the self-energy after the first iteration takes the usual *GW* form, from which the already included static exchange and correlation effects (due to V_{xc}) need to be subtracted in Eq.(3.111), i.e. $\Sigma^{xc} \rightarrow \Sigma^{xc} - V_{xc}$. On the other hand, the calculation of the quasiparticle energy [Eq.(3.81)] requires a self-consistent solution, since the self-energy itself depends on the latter one. This is achieved iteratively by use of the Newton-Raphson method as follows:

$$E_{\mathbf{k}}^{\text{qp},N+1} = E_{\mathbf{k}}^{\text{qp},N} + Z_{\mathbf{k}} \Re \left[\Sigma_{\mathbf{k}\mathbf{k}}^{\text{xc}}(E^{\text{qp},N}/\hbar) - V_{xc,\mathbf{k}\mathbf{k}} \right] \quad \text{and} \quad E_{\mathbf{k}}^{\text{qp},0} \equiv \varepsilon_{\mathbf{k}}, \quad (3.132)$$

where $Z_{\mathbf{k}}$ is the renormalization factor

$$Z_{\mathbf{k}} = \left(1 - \frac{\partial \Re \Sigma_{\mathbf{k}\mathbf{k}}^{\text{xc}}(\omega)}{\partial(\hbar\omega)} \bigg|_{\hbar\omega=E_{\mathbf{k}}^{\text{qp},N}} \right)^{-1}. \quad (3.133)$$

Equation (3.132) is obtained by linearizing the self-energy at the reference energy $\varepsilon_{\mathbf{k}}$, assuming the energy difference $E_{\mathbf{k}}^{\text{qp}} - \varepsilon_{\mathbf{k}}$, which is usually denoted as the *quasiparticle correction*, to be small compared to $\varepsilon_{\mathbf{k}}$. Commonly, the very first iteration of Eq.(3.132) with $N = 0$ is the method of choice to perform the quasiparticle calculation and is known as G_0W_0 . Nevertheless, the quasiparticle energies can be iterated up to any order N meaning an update of the poles of the Green's function. If only the Green's function is updated, one often speaks of a G_NW_0 approximation, while the additional update of the screened potential W due to Eq.(3.130) is denoted as G_NW_N -approximation. What all approximation have in common are fixed orbitals $\varphi_{\mathbf{k}}$ of the reference system. Since the screened potential is kept at the *RPA* level, every iteration in the quasiparticle energy, means an iteration of Hedin's equation without updating the vertex function. Results and discussion of the applicability of the various *GW* flavors [68, 69] are of great interest, in particular, focussing on an improved band gap for semiconductors and insulators [70, 71]. There are methods, however, that go beyond the aforementioned G_NW_N -approximations that include also an update of the orbitals $\varphi_{\mathbf{k}}$ [72, 73, 74]. This quasiparticle self-consistent *GW* approximation considers the solution of the full eigenvalue problem [Eq.(3.85)]²³ and takes also the non-diagonal matrix elements of the Hermitian part of the self-energy into account.

Consequences for the Bethe-Salpeter equation

Through the *GW*-approximation of the self-energy Σ^{xc} , the electron-hole interaction given by the kernel of the BSE for the polarization function and the modified kernel for the density correlation function is directly affected. With Eq.(3.131) and the definition of Ξ [Eq.(3.115)] one finds

$$\Xi(2, 1, 3, 4) = -\frac{\delta [G(12)W(1^+2)]}{\delta G(34)} = -\delta(1-3)\delta(2-4)W(1^+2) - G(12)\frac{\delta W(1^+2)}{\delta G(34)} \quad (3.134)$$

²³The expansion of $\Sigma^{xc}(E_{\mathbf{k}}^{\text{qp}})$ around the reference energy $\varepsilon_{\mathbf{k}}$ in Eq.(3.85) leads to a generalized EVP.

and similarly for Ξ'

$$\Xi'(2, 1, 3, 4) = \frac{\delta [\Sigma_H(12) + \Sigma^{xc}(12)]}{\delta G(34)} = \delta(1-2)\delta(3^+-4)v(1-3) + \Xi(2, 1, 3, 4). \quad (3.135)$$

The variation of the screened potential w.r.t. the Green's function at the rhs of Eq.(3.134) is proportional to W^2 [64] and is usually neglected due to its hopefully little contribution in practical applications but also because of its complexity. Hence the Bethe-Salpeter equation takes a simplified form, which for the density correlation function reads

$$\begin{aligned} L(1, 3, 2, 4) &= L_0(1, 3, 2, 4) \\ &+ \int d5 d6 d7 d8 L_0(1, 3, 6, 5)\delta(5-6)\delta(7-8)v(5-8)L(7, 8, 2, 4) \\ &- \int d5 d6 d7 d8 L_0(1, 3, 6, 5)\delta(5-7)\delta(6-8)W(5^+6)L(7, 8, 2, 4) \end{aligned} \quad (3.136)$$

As already indicated by Eq.(3.126), the density correlation function may be derived from the two-particle Green's function and hence allows a Feynman graph representation. Therefore, one might swap the second and the third argument in $L(1, 3, 2, 4)$ as it can be found e.g. in Ref.[75]. I, however, keep the initial notation to avoid any confusions. With Eq.(3.136) one then obtains the following integral expression

$$\begin{aligned} L(1, 3, 2, 4) &= -i\hbar G(14)G(23) - i\hbar \int d6 d8 G(16)G(63)v(6-8)L(8, 8, 2, 4) \\ &+ i\hbar \int d7 d8 G(17)G(83)W(7^+8)L(7, 8, 2, 4), \end{aligned} \quad (3.137)$$

which has a diagrammatic representation as shown in Fig.(3.6). One notes, that the density correlation function is represented by two Green's function lines heading in opposite directions and thus allow the interpretation of an electron-hole propagation. This comes due to the initial three-point expression of L , i.e. $\lim_{4 \rightarrow 2^+} L(1, 3, 2, 4) = L(1, 3, 2, 2^+)$. Furthermore, one obtains the causal two-point density correlation function, also known as the *polarizability* $\chi(12)$, by contraction of arguments [75]:

$$\chi(12) \equiv L(1, 1^+, 2, 2^+). \quad (3.138)$$

Hence, Eq.(3.137) represents the basic equation to calculate the microscopic density response function, from which the inverse dielectric function ϵ^{-1} is derived. The screened interaction W [Eq.(3.108)] is then usually approximated within the random phase approximation, with the polarization function P [Eq.(3.109)] approximated as $P = GG$.

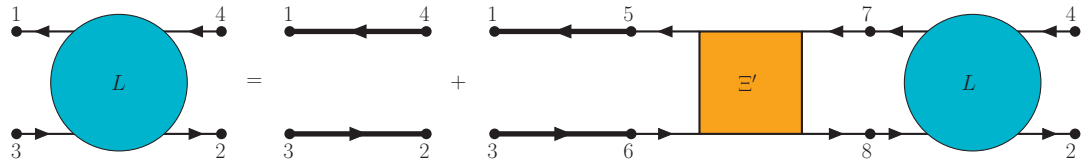


Figure 3.4.: Graphical representation of the Bethe-Salpeter equation for the density-correlation function L due to Eq.(3.124). The thick solid lines display a dressed Green's function.

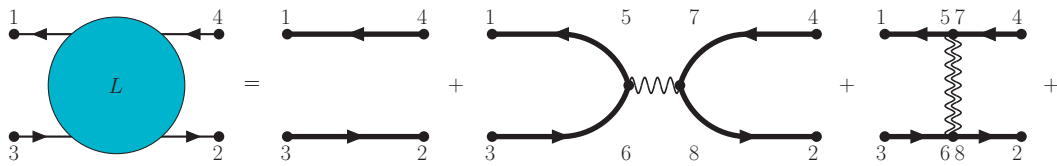


Figure 3.5.: Figure (3.6) with the self-energy approximated by the *GW* approximation. The wiggly line corresponds to the Coulomb interaction, while the double wiggly line represents the screened Coulomb interaction W .

4. Density response formalism

In this section I want to put the time-ordered response function derived from the Green's function formalism into the relation to physical accessible retarded response quantities. Furthermore, the previously introduced microscopic quantities such as the density correlation function L or the polarization function P and related response quantities such as ϵ^{-1} and ϵ would in general require a calculation on an atomic scale. This is, however, an unfeasible task concerning the number of electrons per volume in real systems. Hence, it is convenient to express the microscopic relations by their corresponding macroscopic counterpart, which thus enables us to treat the response of a particular many-particle system on a macroscopic footing. In particular, we are interested in the optical absorption process and hence consider the response within the scale of visible wave lengths. As they lie within the range of $400 \dots 700\text{nm}$, they cannot resolve the microscopic inter-atomic distances of about $\sim 3\text{\AA}$. Finally, the last parts are then devoted to alternative methods that allow to calculate the density response function and subsequently the dielectric function.

4.1. Linear response

Within the framework of the linear response theory we follow the question about the response of a microscopic system that is exposed to a weak external perturbation. As this is a retarded process, one can impose the following form of the resulting Hamiltonian that includes the perturbation $\hat{H}'(t)$ [76, 41]

$$\hat{H}(t) = \hat{H} + \hat{H}'(t)\Theta(t - t_0). \quad (4.1)$$

Here, we denote the many-body Hamiltonian [Eq.(2.1)] by $\hat{H}$ and the theta function suddenly switches on the perturbation at the time point t_0 . Considering the initial many-particle state $|\Psi(t_0)\rangle$, its time evolution under the influence of the perturbation is then governed by the corresponding time evolution operator $U(t, t_0)$ [Eq.(D.9)]. To first order in the perturbation one thus finds

$$|\tilde{\Psi}(t)\rangle = \left[e^{-\frac{i}{\hbar}\hat{H}(t-t_0)} + \frac{1}{i\hbar} \int_{t_0}^t dt' e^{-\frac{i}{\hbar}\hat{H}(t-t')} \hat{H}'(t') e^{-\frac{i}{\hbar}\hat{H}(t'-t_0)} \right] |\Psi(t_0)\rangle. \quad (4.2)$$

The response of the considered systems is now manifested by the change of an observable measured with and without the external perturbation. Hence one needs to calculate the difference $\langle \tilde{\Psi}(t) | \hat{O}(t) | \tilde{\Psi}(t) \rangle - \langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle$. From Eq.(4.2) one deduces the following expression of the expectation value of the observable $\hat{O}(t)$ at the time point t if the factor proportional to the

square to $\hat{H}'$ is neglected:

$$\begin{aligned} \langle \tilde{\Psi}(t) | \hat{O}(t) | \tilde{\Psi}(t) \rangle &= \left\langle \Psi(t_0) \left| e^{\frac{i}{\hbar} \hat{H}(t-t_0)} \hat{O}(t) e^{-\frac{i}{\hbar} \hat{H}(t-t_0)} \right| \Psi(t_0) \right\rangle \\ &+ \left\langle \Psi(t_0) \left| \frac{1}{i\hbar} \int_{t_0}^t dt' e^{\frac{i}{\hbar} \hat{H}(t-t_0)} \hat{O}(t) e^{-\frac{i}{\hbar} \hat{H}(t-t')} \hat{H}'(t') e^{-\frac{i}{\hbar} \hat{H}(t'-t_0)} \right| \Psi(t_0) \right\rangle \\ &- \left\langle \Psi(t_0) \left| \frac{1}{i\hbar} \int_{t_0}^t dt' e^{\frac{i}{\hbar} \hat{H}(t'-t_0)} \hat{H}'(t') e^{\frac{i}{\hbar} \hat{H}(t-t')} \hat{O}(t) e^{-\frac{i}{\hbar} \hat{H}(t-t_0)} \right| \Psi(t_0) \right\rangle. \end{aligned} \quad (4.3)$$

The first term in the equation above simply yields the expectation value of the unperturbed state $|\Psi(t)\rangle$ at the time point t , so that the change of the observable $\hat{O}(t)$ caused by the perturbation $\hat{H}'(t)$ is then given by

$$\langle \tilde{\Psi}(t) | \hat{O}(t) | \tilde{\Psi}(t) \rangle - \langle \Psi(t) | \hat{O}(t) | \Psi(t) \rangle = \frac{1}{i\hbar} \int_{t_0}^t dt' \left\langle \Psi_0 \left| \left[\hat{O}_H(t), \hat{H}'_H(t') \right] \right| \Psi_0 \right\rangle. \quad (4.4)$$

The operators at the rhs are represented within the Heisenberg picture wrt to the many-particle Hamiltonian $\hat{H}$, which is denoted by the index H. Furthermore, the remaining exponential factors $e^{\pm \frac{i}{\hbar} \hat{H}(t-t_0)}$ in Eq.(4.3) transform the state $|\Psi(t_0)\rangle$ (respectively the c.c.) back to the time point $t_0 = 0$ and thus to the unperturbed and initial ground state $|\Psi_0\rangle$. As we want to study the response that couples to the density ρ , the external perturbation may be written as an external potential and thus reads

$$\hat{H}'(t) = \int d\mathbf{r} \hat{\rho}(\mathbf{r}) \tilde{V}(\mathbf{r}, t). \quad (4.5)$$

If one seeks for the density variation one immediately finds

$$\delta\rho(\mathbf{r}, t) = \frac{1}{i\hbar} \int_{t_0}^t dt' \int d\mathbf{r}' \left\langle \Psi_0 \left| \left[\hat{\rho}_H(\mathbf{r}t), \hat{\rho}'_H(\mathbf{r}'t') \right] \right| \Psi_0 \right\rangle \tilde{V}(\mathbf{r}', t'). \quad (4.6)$$

The commutator, however, may be rewritten, if one substitutes the density operator with the aid of the density deviation operator [50] $\Delta\hat{\rho}(\mathbf{r}t) \equiv \hat{\rho}(\mathbf{r}t) - \langle \Psi_0 | \hat{\rho}(\mathbf{r}t) | \Psi_0 \rangle$ that measures the density fluctuation around the ground state density. Thus, Eq.(4.6) takes the final form

$$\delta\rho(\mathbf{r}, t) = \int_{-\infty}^{\infty} dt' \int d\mathbf{r}' \chi^{\text{ret}}(\mathbf{r}t, \mathbf{r}'t') \tilde{V}(\mathbf{r}', t'), \quad (4.7)$$

where χ^{ret} denotes the *retarded* density-density correlation function:

$$\chi^{\text{ret}}(\mathbf{r}t, \mathbf{r}'t') = \frac{1}{i\hbar} \Theta(t - t') \left\langle \Psi_0 \left| \left[\Delta\hat{\rho}_H(\mathbf{r}t), \Delta\hat{\rho}'_H(\mathbf{r}'t') \right] \right| \Psi_0 \right\rangle. \quad (4.8)$$

By inspection of the time-ordered density correlation functions [Eq.(3.118)], both functions, χ^{ret} and L simply differ by the different time arguments in the theta functions. This, however,

restricts the possible calculation of the density correlation function with the aid of the Wick theorem to the time-ordered quantity L . The question in what way both quantities can be related to each other, is seen by their Fourier transformation.

4.1.1. Analytical properties of χ^{ret}

The transition to the frequency domain can be performed following the definition in Eq.(C.1) and taking into account the representation of the theta function $\Theta(t - t_0)$ [Eq.(C.2)]. Since the many-particle Hamiltonian $\hat{H}$ is homogenous in time, the retarded density correlation function, defined in the Heisenberg picture w.r.t $\hat{H}$, thus depends on the time difference $t - t'$ only and becomes a function of one frequency argument. Correspondingly, one obtains the frequency component $\chi^{\text{ret}}(\omega)$ as the following

$$\chi^{\text{ret}}(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\eta \rightarrow 0} \sum_{\beta \neq 0} \left[\frac{\langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_\beta \rangle \langle \Psi_\beta | \hat{\rho}(\mathbf{r}') | \Psi_0 \rangle}{\hbar\omega - (E_\beta - E_0) + i\hbar\eta} - \frac{\langle \Psi_0 | \hat{\rho}(\mathbf{r}') | \Psi_\beta \rangle \langle \Psi_\beta | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle}{\hbar\omega + (E_\beta - E_0) + i\hbar\eta} \right]. \quad (4.9)$$

The summation at the rhs explicitly excludes the ground state with index $\beta = 0$ because of the density deviation operator. Moreover, the same analysis as for $\chi^{\text{ret}}(\omega)$ would yield the (contracted) causal density correlation function $\chi(\omega) \equiv L(\omega)$, which in the end differs only by the complex term in the second term of the rhs of Eq.(4.9), i.e. one simply has to substitute $+i\eta \rightarrow -i\eta$. Nevertheless, both quantities yield the same excitation energies $\hbar\Omega_\beta = E_\beta - E_0$, which lie completely below the real frequency axis in case of $\chi^{\text{ret}}(\omega)$ and otherwise are located below the same axis for positive frequencies and above for negative frequencies, respectively. Hence for positive real frequencies, i.e. $\omega \geq 0$, one finds that $\chi^{\text{ret}}(\omega) = L(\omega)$. One may additionally note that compared to the Lehman representation of the time-ordered Green's function [see Eq.(E.6)], the Lehman representation of $\chi^{\text{ret}}(\omega)$ or that of $L(\omega)$ differ by the minus sign between the two terms in Eq.(4.9), which is due to the bosonic character of the density operator in contrast to the fermionic character of the field operators in the definition of the Green's function. Considering the summation in Eq.(4.9) one identifies the many-particle state Ψ_β to be an N -particle state, due to the definition of the density operator $\hat{\rho}$. Hence, the density fluctuation response function describes neutral excitations of a many-particle system, exactly those excitation, which are the main topic of this work.

4.1.2. Independent particle approximation for χ ($T = 0$)

Similarly to the analysis of the determination of the Green's function in terms of Feynman diagrams, the time-ordered density correlation function χ may also be written as a perturbation series in terms of the Coulomb interaction $\hat{V}_{\text{int}}$. I follow closely [51] and [50]. By analogy of the procedure of deriving the Feynman graph representation for the Green's function [Eq.(3.68)], the

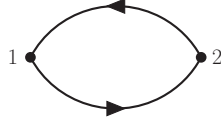


Figure 4.1.: Feynman graph for $\chi_0(1,2)$. The thin black lines denote the independent particle Green's function.

correlation function χ has the following series expansion

$$i\hbar \chi(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \left\langle \Phi_0 \left| \sum_{l=0}^{\infty} \left(\frac{-i}{\hbar} \right)^l \frac{1}{l!} \int_{-\infty}^{\infty} dt'_1 \dots \int_{-\infty}^{\infty} dt'_l \right. \right. \\ \left. \times \mathcal{T} \left[\hat{V}_{\text{int,I}}(t'_1) \dots \hat{V}_{\text{int,I}}(t'_l) \hat{\rho}_I(\mathbf{r}_1 t_1) \hat{\rho}_I(\mathbf{r}_2 t_2) \right] \right| \Phi_0 \rangle_{\text{fully connected}}. \quad (4.10)$$

The expansion above is expressed in terms of the density operator instead of the corresponding deviation density operator, which can be done, because one can proof that $[\hat{\rho}(1), \hat{\rho}(2)] = [\Delta\hat{\rho}(1), \Delta\hat{\rho}(2)]$ holds¹. We will give now the explicit expression for the independent particle approximation of the density correlation function χ_0 that is derivable from the first term $l = 0$ of Eq.(4.10). One thus finds with the definition of the density operator, i.e. $\hat{\rho}(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r})\hat{\psi}(\mathbf{r})$, the time ordered expression

$$i\hbar \chi_0(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \left\langle \Phi_0 \left| \mathcal{T} \left[\hat{\psi}_I^\dagger(\mathbf{r}_1 t_1) \hat{\psi}_I(\mathbf{r}_1 t_1) \hat{\psi}_I^\dagger(\mathbf{r}_2 t_2) \hat{\psi}_I(\mathbf{r}_2 t_2) \right] \right| \Phi_0 \right\rangle, \quad (4.11)$$

which can be further formulated as the sum over all contractions due to the Wick theorem. Therefore only contributions with contractions of one creation and one destruction field operator remain. Hence, Eq.(4.11) may be rewritten as the following:

$$i\hbar \chi_0(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \overbrace{\hat{\psi}_I(\mathbf{r}_1 t_1) \hat{\psi}_I^\dagger(\mathbf{r}_1 t_1)} \overbrace{\hat{\psi}_I(\mathbf{r}_2 t_2) \hat{\psi}_I^\dagger(\mathbf{r}_2 t_2)} - \overbrace{\hat{\psi}_I(\mathbf{r}_1 t_1) \hat{\psi}_I^\dagger(\mathbf{r}_2 t_2)} \overbrace{\hat{\psi}_I(\mathbf{r}_2 t_2) \hat{\psi}_I^\dagger(\mathbf{r}_1 t_1)}. \quad (4.12)$$

The first term on the rhs of Eq.(4.12) simply yields two unconnected fermionic loops and thus drops out. What remains is a product of two contractions, the second term on the rhs, that can be identified as the product of two non-interacting Green's functions G_0 . Consequently, the independent particle approximation for the density correlation function then reads

$$\chi_0(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = -i\hbar G_0(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) G_0(\mathbf{r}_2 t_2, \mathbf{r}_1 t_1) \quad (4.13)$$

In terms of a Feynman diagram, χ_0 is represented by a so called 'bubble'-diagram as shown in Fig(4.1.2).

¹One substitute the density operator by $\Delta\hat{\rho} + \langle\hat{\rho}\rangle$ and calculates the commutator, taking into account that $\langle\rho\rangle$ is a complex number and complex numbers always commute.

4.1.3. Fourier transformation and Bloch representation of χ_0

At this point it proves beneficial to switch from the time domain into the frequency domain in order to find the excitation energies Ω_β of the independent particle response function χ_0 . On the other hand, the Fourier transformation from real space to the momentum domain allows to discuss the coupling of the external potential via the density response function in terms of plane waves with the many-particle system. Starting with the Fourier transform $\chi_0(\omega)$ we find using Eq.(C.1)

$$\begin{aligned}
\chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega) &= -i\hbar \int_{-\infty}^{\infty} dt e^{i\omega(t_1-t_2)} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega_1 e^{-i\omega_1(t_1-t_2)} G_0(\mathbf{r}_1, \mathbf{r}_2; \omega_1) \\
&\quad \times \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega_2 e^{-i\omega_2(t_2-t_1)} G_0(\mathbf{r}_1, \mathbf{r}_2; \omega_2) \\
&= -i\hbar \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega_1 d\omega_2 G_0(\mathbf{r}_1, \mathbf{r}_2; \omega_1) G_0(\mathbf{r}_1, \mathbf{r}_2; \omega_2) \delta(\omega - \omega_1 + \omega_2) \\
&= -i\hbar \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega_2 G_0(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega_2) G_0(\mathbf{r}_1, \mathbf{r}_2; \omega_2).
\end{aligned} \tag{4.14}$$

Obviously, the frequency component $\chi_0(\omega)$ depends on an additional frequency ω_2 that, however, can be eliminated if one considers the explicit expression for Green's function for real frequencies $G_0(\omega)$. Since $G_0(\omega)$ has poles above and below the real frequency axis, the integral in the last line of Eq.(4.14) can be evaluated as a contour integral that is closed either in the upper or lower half complex plane. It yields two non-vanishing contributions and one obtains

$$\begin{aligned}
\chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega) &= \sum_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2} \varphi_{\tilde{\mathbf{k}}_1}(\mathbf{r}_1) \varphi_{\tilde{\mathbf{k}}_1}^*(\mathbf{r}_2) \varphi_{\tilde{\mathbf{k}}_2}(\mathbf{r}_2) \varphi_{\tilde{\mathbf{k}}_2}^*(\mathbf{r}_1) \\
&\quad \times \left[\frac{\Theta(\varepsilon_{\tilde{\mathbf{k}}_1} - \varepsilon_F) \Theta(\varepsilon_F - \varepsilon_{\tilde{\mathbf{k}}_2})}{\hbar\omega + \varepsilon_{\tilde{\mathbf{k}}_2} - \varepsilon_{\tilde{\mathbf{k}}_1} + i\hbar\eta} - \frac{\Theta(\varepsilon_F - \varepsilon_{\tilde{\mathbf{k}}_1}) \Theta(\varepsilon_{\tilde{\mathbf{k}}_2} - \varepsilon_F)}{\hbar\omega + \varepsilon_{\tilde{\mathbf{k}}_2} - \varepsilon_{\tilde{\mathbf{k}}_1} - i\hbar\eta} \right]
\end{aligned} \tag{4.15}$$

where ε_F denotes the Fermi energy. As the Green's function is supposed to have a lattice symmetry², and thus $\chi_0(\mathbf{r}_1, \mathbf{r}_2)$, the transition to the momentum domain is then obtained by

$$\chi_0(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'; \omega) = \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}_1} \chi_0(\mathbf{r}_1, \mathbf{r}_2; \omega) e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}_2}, \tag{4.16}$$

where $\mathbf{q}$ is a vector of the first Brillouin zone and V denotes the crystal volume. Hence, with Eq.(4.15) we find the corresponding representation of χ_0 in reciprocal momentum space as the

²A lattice symmetric function $f(\mathbf{r}_1, \mathbf{r}_2)$ coincide with $f(\mathbf{r}_1 + \mathbf{R}, \mathbf{r}_2 + \mathbf{R})$ if $\mathbf{R}$ is a Bravais lattice vector.

following

$$\begin{aligned} \chi_0(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'; \omega) = & \frac{1}{V} \sum_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2} B_{\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1*}(\mathbf{q} + \mathbf{G}) B_{\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1}(\mathbf{q} + \mathbf{G}') \\ & \times \left[\frac{\Theta(\varepsilon_{\tilde{\mathbf{k}}_1} - \varepsilon_F) \Theta(\varepsilon_F - \varepsilon_{\tilde{\mathbf{k}}_2})}{\hbar\omega + \varepsilon_{\tilde{\mathbf{k}}_2} - \varepsilon_{\tilde{\mathbf{k}}_1} + i\hbar\eta} - \frac{\Theta(\varepsilon_F - \varepsilon_{\tilde{\mathbf{k}}_1}) \Theta(\varepsilon_{\tilde{\mathbf{k}}_2} - \varepsilon_F)}{\hbar\omega + \varepsilon_{\tilde{\mathbf{k}}_2} - \varepsilon_{\tilde{\mathbf{k}}_1} - i\hbar\eta} \right]. \end{aligned} \quad (4.17)$$

Here we have introduced the Bloch integrals defined as

$$B_{\mathbf{k}_2}^{\tilde{\mathbf{k}}_1}(\mathbf{q} + \mathbf{G}) \equiv B_{(n_2 \mathbf{k}_2)}^{(n_1 \mathbf{k}_1)}(\mathbf{q} + \mathbf{G}) := \int_V d\mathbf{r} \varphi_{n_1 \mathbf{k}_1}^*(\mathbf{r}) e^{i(\mathbf{q} + \mathbf{G})\mathbf{r}} \varphi_{n_2 \mathbf{k}_2}(\mathbf{r}). \quad (4.18)$$

With the definition of the Bloch orbitals [Eq.(3.53)], the integral on the rhs of Eq.(4.18) reduces to

$$B_{(n_2 \mathbf{k}_2)}^{(n_1 \mathbf{k}_1)}(\mathbf{q} + \mathbf{G}) = \delta_{\mathbf{k}_1, \mathbf{k}_2 + \mathbf{q}} \frac{1}{V_0} \int_{V_0} d\mathbf{r} u_{n_1 \mathbf{k}_1}^*(\mathbf{r}) e^{i\mathbf{G}\mathbf{r}} u_{n_2 \mathbf{k}_2}(\mathbf{r}).^3 \quad (4.19)$$

The Bloch integral thus describes the transition from a state with momentum $\mathbf{k}_2$ to the state $\mathbf{k}_2 + \mathbf{q} + \mathbf{G}$ under the influence of an external perturbation $e^{i(\mathbf{q} + \mathbf{G})\mathbf{r}}$ and thus implies the momentum conservation rule $\mathbf{k}_1 = \mathbf{k}_2 + \mathbf{q}$. In the limiting case $\mathbf{q} = 0$ momentum conservation then restricts that $\mathbf{k}_1 = \mathbf{k}_2$ and thus vertical transitions (within the picture of the corresponding band structure) need to be taken into account only.

Long wave length limit $\mathbf{q} \rightarrow 0$

At the interesting case of an external perturbation due to an optical wave vector with vanishing momentum $\mathbf{q} \rightarrow 0$, the Bloch integral

$$\lim_{\mathbf{q} \rightarrow 0} B_{(n_2 \mathbf{k}_2)}^{(n_1 \mathbf{k}_2 + \mathbf{q})}(\mathbf{q}) = \lim_{\mathbf{q} \rightarrow 0} \int_V d\mathbf{r} \varphi_{n_1 \mathbf{k}_2 + \mathbf{q}}^*(\mathbf{r}) e^{i\mathbf{q}\mathbf{r}} \varphi_{n_2 \mathbf{k}_2}(\mathbf{r}) \quad (4.20)$$

needs to be evaluated. This might be done by a Taylor series expansion of the exponential around $\mathbf{q} = 0$ and thus yields the dipol approximation of Eq.(4.20) with the dipol moment $i\mathbf{q} \langle n_1 \mathbf{k}_2 + \mathbf{q} | \mathbf{r} | n_2 \mathbf{k}_2 \rangle$. This matrix element, however, becomes difficult to solve if periodic boundary conditions need to be considered. Instead, one may evaluate the matrix element of the commutator $[e^{i\mathbf{q}\mathbf{r}}, \hat{H}]$ with the Hamiltonian separated as $\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m_e} + \hat{V}_{\text{loc}} + \hat{V}_{\text{nl}}$, where the potential terms are divided into a local $\hat{V}_{\text{loc}}$ and a non-local part $\hat{V}_{\text{nl}}$. With the orbitals $\varphi_{n\mathbf{k}}$ being eigenstates of $\hat{H}$ one finds on the one hand

$$\langle n_1 \mathbf{k}_2 + \mathbf{q} | [e^{i\mathbf{q}\mathbf{r}}, \hat{H}] | n_2 \mathbf{k}_2 \rangle = (\varepsilon_{n_2 \mathbf{k}_2} - \varepsilon_{n_1 \mathbf{k}_2 + \mathbf{q}}) \langle n_1 \mathbf{k}_2 + \mathbf{q} | e^{i\mathbf{q}\mathbf{r}} | n_2 \mathbf{k}_2 \rangle, \quad (4.21)$$

³Here V_0 denotes the unit cell volume and $u_{n\mathbf{k}}(\mathbf{r})$ is the cell periodic part of the Bloch orbital $\varphi_{n\mathbf{k}}(\mathbf{r})$.

while on the other hand the commutator is given by [47]

$$\left[e^{i\mathbf{q}\mathbf{r}}, \hat{H} \right] = -\frac{\hbar\mathbf{q}}{m_e} \hat{\mathbf{p}} e^{i\mathbf{q}\mathbf{r}} + \frac{\hbar^2 q^2}{2m_e} e^{i\mathbf{q}\mathbf{r}} + \left[e^{i\mathbf{q}\mathbf{r}}, \hat{V}_{\text{nl}} \right]. \quad (4.22)$$

Thus from Eq.(4.21) and Eq.(4.22) one obtains

$$\begin{aligned} & \langle n_1 \mathbf{k}_2 + \mathbf{q} | e^{i\mathbf{q}\mathbf{r}} | n_2 \mathbf{k}_2 \rangle \\ &= \left(\varepsilon_{n_1 \mathbf{k}_2 + \mathbf{q}} - \varepsilon_{n_2 \mathbf{k}_2} + \frac{\hbar^2 q^2}{2m_e} \right)^{-1} \frac{\hbar}{m_e} \langle n_1 \mathbf{k}_2 + \mathbf{q} | \mathbf{q} \hat{\mathbf{p}} | n_2 \mathbf{k}_2 \rangle + \langle n_1 \mathbf{k}_2 + \mathbf{q} | \left[e^{i\mathbf{q}\mathbf{r}}, \hat{V}_{\text{nl}} \right] | n_2 \mathbf{k}_2 \rangle. \end{aligned} \quad (4.23)$$

At this point the limes $\mathbf{q} \rightarrow 0$ can be taken if both sides are manipulated with a factor $1/|\mathbf{q}|$ that introduces the unit vector $\hat{\mathbf{q}} = \frac{\mathbf{q}}{|\mathbf{q}|}$. We thus define the optical matrix element as the following

$$\begin{aligned} M_{n_2 \mathbf{k}_2}^{n_1 \mathbf{k}_2}(\hat{\mathbf{q}}) &:= \lim_{\mathbf{q} \rightarrow 0} \frac{1}{|\mathbf{q}|} B_{n_2 \mathbf{k}_2}^{n_1 \mathbf{k}_2 + \mathbf{q}}(\mathbf{q}) \\ &= \frac{\hbar \hat{\mathbf{q}}}{m_e} \frac{\langle n_1 \mathbf{k}_2 | \hat{\mathbf{p}} | n_2 \mathbf{k}_2 \rangle}{(\varepsilon_{n_1 \mathbf{k}_2} - \varepsilon_{n_2 \mathbf{k}_2})} - \frac{i \hat{\mathbf{q}} \langle n_1 \mathbf{k}_2 | [\mathbf{r}, \hat{V}_{\text{nl}}] | n_2 \mathbf{k}_2 \rangle}{(\varepsilon_{n_1 \mathbf{k}_2} - \varepsilon_{n_2 \mathbf{k}_2})} \end{aligned} \quad (4.24)$$

with the unit vector $\hat{\mathbf{q}}$ indicating the direction of the incident wave vector. The commutator of the non-local potential needs to be evaluated separately. Alternatively, Eq.(4.24) would have been obtained, if we evaluated the limit $\lim_{\mathbf{q} \rightarrow 0} \frac{1}{|\mathbf{q}|} \left[e^{i\mathbf{q}\mathbf{r}}, \hat{H} \right]$ in Eq.(4.22) first, thus yielding the equivalent velocity representation of Eq.(4.24) with the velocity operator [77, 78, 79, 80]

$$\hat{\mathbf{v}} = \frac{\hat{\mathbf{p}}}{m_e} - \frac{i}{\hbar} [\mathbf{r}, \hat{V}_{\text{nl}}]. \quad (4.25)$$

4.1.4. Retarded dielectric function of independent particles

With regard to the definition of the dielectric function and its inverse one immediately verifies that within the independent particle approximation, the density correlation function and the polarization function are equivalent, i.e. $L^{\text{ip}} = P^{\text{ip}} \equiv \chi_0$. Thus the dielectric function is obtained from Eq.(3.123), which in reciprocal space takes the form [c.f. Eq.(H.3)]

$$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}; \omega) = \delta_{\mathbf{G}\mathbf{G}'} - v(\mathbf{q} + \mathbf{G}) P^{\text{ip}}(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'; \omega). \quad (4.26)$$

However, the physical accesible quantities are just retarded quantities and one needs to find the corresponding retarded expression for the independent particle approximation of χ_0 . This can be easily achieved if one switches the complex term $-i\eta$ to $i\eta$ in Eq.(4.17). What remains is a common nominator of the type $\Theta(\varepsilon_{\tilde{\mathbf{k}}_1} - \varepsilon_{\text{F}}) \Theta(\varepsilon_{\text{F}} - \varepsilon_{\tilde{\mathbf{k}}_2}) - \Theta(\varepsilon_{\text{F}} - \varepsilon_{\tilde{\mathbf{k}}_1}) \Theta(\varepsilon_{\tilde{\mathbf{k}}_2} - \varepsilon_{\text{F}})$ that obviously can be reduced to $\Theta(\varepsilon_{\text{F}} - \varepsilon_{\tilde{\mathbf{k}}_2}) - \Theta(\varepsilon_{\text{F}} - \varepsilon_{\tilde{\mathbf{k}}_1})$. Hence the resulting retarded microscopic dielectric function of independent particles can be calculated with the corresponding retarded expression

of P^{ip} in Eq.(4.26) and reads

$$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}; \omega) = \delta_{\mathbf{G}\mathbf{G}'} - \frac{4\pi e^2}{|\mathbf{q} + \mathbf{G}|^2} \sum_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2} B_{\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1*}(\mathbf{q} + \mathbf{G}) B_{\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1}(\mathbf{q} + \mathbf{G}') \frac{\Theta(\varepsilon_F - \varepsilon_{\tilde{\mathbf{k}}_2}) - \Theta(\varepsilon_F - \varepsilon_{\tilde{\mathbf{k}}_1})}{\hbar\omega + \varepsilon_{\tilde{\mathbf{k}}_2} - \varepsilon_{\tilde{\mathbf{k}}_1} + i\hbar\eta} \quad (4.27)$$

Equation (4.27) has been also independently derived by Adler[81] and Wiser [82] within the self-consistent field methods. Even in the simplest approximation of the microscopic dielectric function one observes that in reciprocal space $\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q})$ is a matrix of the reciprocal lattice vectors $\mathbf{G}$. This is due to the fact that the microscopic dielectric function in real space $\epsilon(\mathbf{r}, \mathbf{r}')$ is non-local and thus takes into account all inhomogeneities on the microscopic scale. Within the concept of an external perturbation the response function χ determines the induced density [see Eq.(4.7)] that gives rise to induced microscopic fields at every spatial point and are usually denoted as *local fields*. Their inclusion requires to keep the Fourier components with $\mathbf{G} \neq 0, \mathbf{G}' \neq 0$ in the microscopic dielectric function of Eq.(4.27). If local fields effect are neglected, i.e. $\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \epsilon_{00}(\mathbf{q})$, one obtains the Ehrenreich-Cohen formula [83]. It further simplifies to the Lindhard-function if the electrons are considered as free moving particles in the presence of an homogenous background, such as in the homogenous electron gas. In this case the orbitals $\varphi_{\tilde{\mathbf{k}}}(\mathbf{r})$ become simply plane waves and the Bloch integrals reduce to simple delta functions, namely $B_{\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1}(\mathbf{q}) = \delta_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2 + \mathbf{q}}$. At the end of this section we want to discuss a special case of the dielectric function, namely that of a vanishing momentum vector $\mathbf{q}$. Following the formulas derived above, Eq.(4.24) and Eq.(4.27) then yields

$$\begin{aligned} \lim_{\mathbf{q} \rightarrow 0} \epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) &= 1 - \lim_{\mathbf{q} \rightarrow 0} v(\mathbf{q}) P_{00}^{\text{ip}}(\mathbf{q}) \\ &= 1 - \frac{4\pi e^2 \hbar^2}{V} \sum_{\mathbf{k}, n_1, n_2} \frac{|\langle n_1 \mathbf{k} | \hat{\mathbf{q}} \hat{\mathbf{v}} | n_2 \mathbf{k} \rangle|^2}{(\varepsilon_{n_1 \mathbf{k}_2} - \varepsilon_{n_2 \mathbf{k}_2})^2} \frac{\Theta(\varepsilon_F - \varepsilon_{n_2 \mathbf{k}_2}) - \Theta(\varepsilon_F - \varepsilon_{n_1 \mathbf{k}_2})}{\hbar\omega + \varepsilon_{n_2 \mathbf{k}_2} - \varepsilon_{n_1 \mathbf{k}_2} + i\hbar\eta}. \end{aligned} \quad (4.28)$$

The fact that we treat the dielectric function in Eq.(4.28) as a response function due to an external potential with vanishing momentum vector $\mathbf{q} = 0$ is only possible if local field effects are neglected. In general, one has to invert the inverse dielectric function $\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q})$ first and then take the limit $\mathbf{q} \rightarrow 0$. If, however, the Fourier components $\epsilon_{\mathbf{G} \neq 0 \mathbf{G}' \neq 0}$ are set to zero, the matrix of the inverse dielectric function is equal to its inverse, and hence one finds $\frac{1}{\epsilon_{00}^{-1}(\mathbf{q})} = \epsilon_{00}(\mathbf{q})$. Since ϵ^{-1} couples the induced microscopic fields to the externally applied field, the neglect of the Fourier components $\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}$ means to disregard this particular coupling to local fields and thus considers only the coupling between the (macroscopic) external field with the macroscopic or averaged microscopic fields of the sample. For real applications, the macroscopic dielectric function is the quantity that is accessible and we will discuss its calculation in section 4.1.8 and chapter 7. Before I do that, one needs to answer the question about the calculation of the microscopic dielectric function that goes beyond the independent particle approximation.

4.1.5. Beyond the independent particle approximation of χ ($T = 0$)

In order to find approximations of the density response function χ that go beyond χ_0 we want to discuss its corresponding approximation to first order, $\chi^{(1)}$, w.r.t. the Coulomb interaction. From Eq.(4.10) one initially finds with $l = 1$:

$$\begin{aligned}
 i\hbar\chi^{(1)}(\mathbf{r}_1t_1, \mathbf{r}_2t_2) = & \left\langle \Phi_0 \left| \left(\frac{-i}{\hbar} \right) \frac{1}{2} \sum_{\substack{\sigma_1, \sigma_2 \\ \sigma'_1, \sigma'_2}} \int_{-\infty}^{\infty} dt'_1 dt'_2 \int d\mathbf{r}'_1 d\mathbf{r}'_2 \right. \right. \\
 & \mathcal{T} \left[\hat{\psi}_1^\dagger(\mathbf{r}'_1t'_1) \hat{\psi}_1^\dagger(\mathbf{r}'_2t'_2) v(\mathbf{r}'_1, \mathbf{r}'_2; t'_1, t'_2) \hat{\psi}_1(\mathbf{r}'_2t'_2) \hat{\psi}_1(\mathbf{r}'_1t'_1) \right. \\
 & \left. \left. \times \hat{\psi}_1^\dagger(\mathbf{r}_1t_1) \hat{\psi}_1(\mathbf{r}_1t_1) \hat{\psi}_1^\dagger(\mathbf{r}_2t_2) \hat{\psi}_1(\mathbf{r}_2t_2) \right] \right| \Phi_0 \rangle \delta_{\sigma_1, \sigma_2}.
 \end{aligned} \tag{4.29}$$

Applying Wick's theorem, the time-ordered product of field operators yields 24 contractions from which only 12 Feynman diagrams are fully connected. Among those 12 diagrams one finds one reducible polarization part [Fig.(4.1.5a)] as well as one irreducible polarization part [Fig.(4.1.5b)]. Additionally, self-energy insertions in the form of skeleton diagrams appear such as shown in figure (4.1.5(c)) and figure (4.1.5(d)). The latter one, also known as the Tadpole-diagram, yields the Hartree energy, while in figure (4.1.5(c)) the corresponding red diagram displays the exchange energy. Both diagrams (c) and (d) appear in two topological equivalent representations and thus need to be counted twice. Furthermore, the same skeleton diagrams are obtained also for the Green's function line heading in the opposite direction. Thus, following the principle of partial summation of repetitive self-energy insertions, we can replace the single non-interacting Green's function line by its dressed counterpart, which is, retaining the Hartree energy and the exchange diagram only, equivalent to the Hartree-Fock approximation of G .⁴ However, at higher orders $l > 1$, the Coulomb line in figure (c), being the lowest order of the so-called polarization diagrams, will be replaced by higher order polarization diagrams giving rise to an effective or dressed interaction. Possible polarization diagrams consist of any polarization parts, connected by an incoming and outgoing Coulomb line. By a partial summation over all possible polarization diagrams, the Coulomb line could be replaced by the full screened interaction W_0 . The index 0 denotes that the screened interaction is obtained by the non-interacting Green's function G_0 . This replacement of the interaction line can, however, be done only for the exchange diagram and not for the Tadpole-diagram in figure (d). For this diagram, the insertion of polarization diagrams would yield so-called anomalous diagrams that cannot occur as they violate momentum conservation [84]. Hence, one would obtain a screened exchange skeleton diagram with a non-interacting Green's function line. The summation of (c) and (d) including the repetitive collocation of the screened exchange diagram in (c) and the repetitive Tadpol-diagram in (d), at every orders of l , yields a single polarization part with a dressed Green's function line as sketched in figure (c')⁵. In general, just a certain class of polarization diagrams is considered giving rise to different approximations to W . In particular, the restriction to the

⁴A dressed Green's function line assumes a self-consistent solution of the self-energy.

⁵Here, the dressed line representing the Green's function is the solution of the Dyson equation with the self-energy approximated by $\Sigma^{\text{xc}} \approx G_0 W_0$

bubble diagram shown in Fig. (4.1.2) yields the random phase approximation of W . For our purposes and within the ordinary GW -calculations, this is the method of choice to approximate the screened interaction. Again, a self-consistent solution of $W[G]$ results in the full random phase approximation of the screened interaction and implies a self-consistent solution of G . As both skeleton diagrams will also emerge at the polarization parts in figure (a) and (b) at higher orders $l > 1$, the same arguments to replace the non-interacting Green's function line by its dressed counterpart holds as well. Hence, we can substitute figure (a) and (b) with the corresponding dressed Green's function lines. One may note that only the irreducible polarization diagram contains a dressed Coulomb line, while the reducible diagram in figure (a') is connected by a bare Coulomb line. In general, any substitution of the bare Coulomb line in Fig. (a') by a dressed interaction line would not yield a new irreducible diagram as this particular one can be always cut into two disjoint polarization parts and one remaining polarization diagram. Eventually, comparing the resulting diagrams (a') and (b') with those diagrams of the four-point density correlation function L , we find the same expressions if and only if one performs the contraction of arguments in $L(1, 3, 2, 4)$, i.e. $3 \rightarrow 1$ and $4 \rightarrow 2$. In other words, the solution of $\chi(1, 2)$ is obtained by the solution of the Bethe-Salpeter equation for L and finally taking the limit as indicated above.

4.1.6. Independent quasiparticle approximation of L

In the previous section we have discussed how to solve the two-point density-response function $\chi(1, 2)$ from a perturbation expansion w.r.t the Coulomb interaction and the screened interaction, respectively. However, as $\chi(1, 2)$ does not obey a Bethe-Salpeter equation like the four point function $L(1, 3, 2, 4)$ due to the non-local interaction $W(1, 2)$ one needs to solve the full BSE, i.e. Eq.(3.137). As we aim to find the two-particle excitation energies, the Fourier coefficients in the frequency domain of the density correlation function need to be calculated. With regard to the four time point arguments of L , it will have three frequency arguments due to three possible time differences. A reduction of this particular time arguments is however possible, since the four point expression of the density correlation function is just a generalization of the original three-point quantity $L(1, 3, 2, 2^+)$ [60].⁶ Therefore we can take without loss of generality the limit $t_4 \rightarrow t_2^+$ to obtain $L(\mathbf{r}_1 t_1, \mathbf{r}_3 t_3, \mathbf{r}_2 t_2, \mathbf{r}_4 t_2^+)$. The transition to the frequency space can now be performed introducing one fermionic Matsubara-frequency z_l and one bosonic Matsubara-frequency ζ_l as the following [85] (the time arguments are complex valued):

$$L(\mathbf{r}_1 t_1, \mathbf{r}_3 t_3, \mathbf{r}_2 t_2, \mathbf{r}_4 t_2^+) = \frac{1}{(-i\hbar\beta)^2} \sum_{l, l'} e^{-iz_{l'}(t_1-t_3)} e^{-i\zeta_l(t_1-t_2)} L(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4; \zeta_l, z_{l'}). \quad (4.30)$$

⁶This particular three point expression is reasoned in the three point vertex Ξ within the corresponding Bethe-Salpeter equation [see Eq. (3.137)].

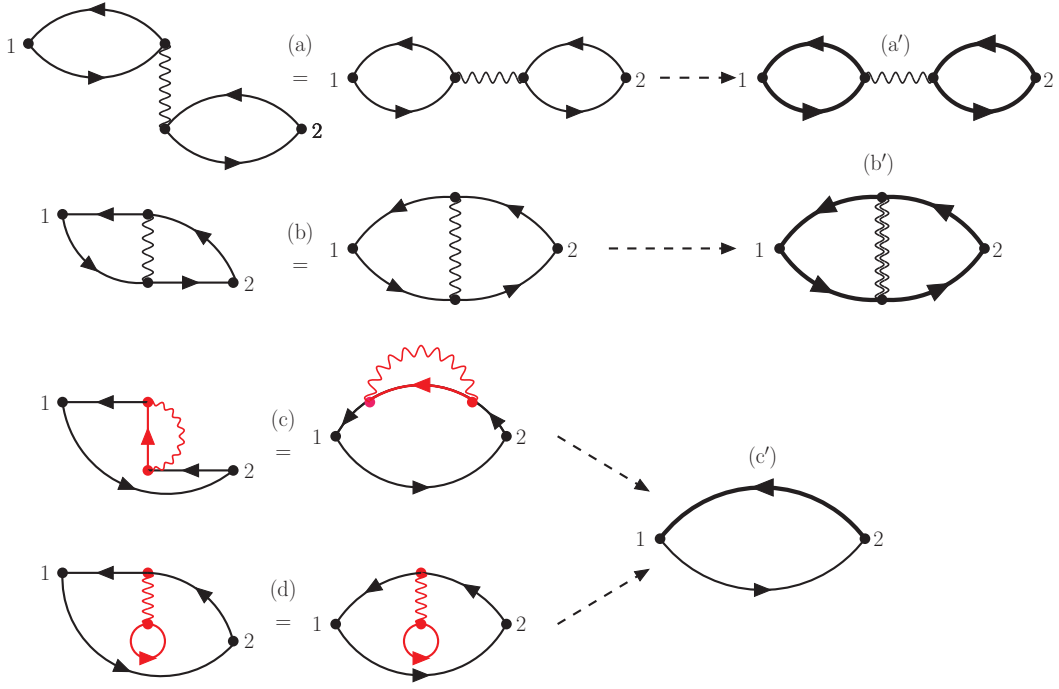


Figure 4.2.: A selection of Feynman diagrams obtained by applying the Wick theorem to the time ordered expression in Eq.(4.29). The non-interacting Green's function is displayed by a thin solid line, while a thick line corresponds to the dressed Green's function. A wiggly line represents the Coulomb interaction v and the double wiggly line denotes the dressed or screened Coulomb interaction W . To the very left side the time-ordered Feynman diagrams are presented to in first order $l = 1$. Since the Coulomb interaction is instantaneous in time, the Coulomb line can be rotated like in figure (a) and (c) to obtain a conformal representation of all Feynman diagrams. In figure (c), the exchange skeleton diagram is shown (red color), while in figure (d) the Tadpole-diagram (red color) is presented. The summation of (c) and (d), including repetitive skeleton diagrams at higher orders $l > 1$, leads to digram (c'). The dressed Green's function line in (c') is either the Hartree-Fock approximation of G or corresponds to G within the GW -approximation of the self-energy $\Sigma = \Sigma^H + \Sigma^{xc,GW}$. Space/time points are abbreviated by $1 = \mathbf{r}, t$.

From the two frequency expression for $L(\zeta_l, z_{l'})$ one can easily obtain the one frequency dependent density correlation function $L(\zeta_l)$ by summation over all fermionic Matsubara-frequencies

$$L(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4; \zeta_l) = \frac{1}{-i\hbar\beta} \sum_{l'} L(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4; \zeta_l, z_{l'}). \quad (4.31)$$

With regard to the solution of the Bethe-Salpeter equation for L in the frequency domain, we have to determine the independent particle approximation of the four-point density-correlation function, i.e. $L_0(1, 3, 2, 4) = G(14)G(23)$. More precisely, as the Green's function is approximated within the quasiparticle formulation, $L_0(1, 3, 2, 4)$ is equivalent to the independent quasiparticle approximation, thus $L_0 = L^{\text{IQPA}}$. With the aid of Eq.(4.30) and the Fourier expansion of the Green's function [Eq.(3.28)] one finds the corresponding expression for $L_0(1, 3, 2, \mathbf{r}_4 t_{2+})$ as the

following

$$L_0(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4; \zeta_l) = \frac{1}{\beta} \sum_{l'} G(\mathbf{r}_1 \mathbf{r}_4; z_{l'} + \zeta_l) G(\mathbf{r}_2 \mathbf{r}_3; z_{l'}). \quad (4.32)$$

In order to resolve the summation over the fermionic frequency we will switch to the Bloch representation of L_0 . According to the expression of the Green's function within the quasiparticle approximation [Eq.(3.87)] it is convenient to express L_0 in a Bloch orbital basis in the following way:

$$L_0(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4; \zeta_l) = \sum_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2, \tilde{\mathbf{k}}_3, \tilde{\mathbf{k}}_4} \varphi_{\tilde{\mathbf{k}}_1}(\mathbf{r}_1) \varphi_{\tilde{\mathbf{k}}_3}^*(\mathbf{r}_3) \varphi_{\tilde{\mathbf{k}}_2}(\mathbf{r}_2) \varphi_{\tilde{\mathbf{k}}_4}^*(\mathbf{r}_4) L_0 \frac{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_3}{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_4}(\zeta_l) \quad (4.33)$$

while the matrix element is defined as

$$L_0 \frac{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_3}{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_4}(\zeta_l) = \iiint \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \varphi_{\tilde{\mathbf{k}}_1}^*(\mathbf{r}_1) \varphi_{\tilde{\mathbf{k}}_3}(\mathbf{r}_3) \varphi_{\tilde{\mathbf{k}}_2}^*(\mathbf{r}_2) \varphi_{\tilde{\mathbf{k}}_4}(\mathbf{r}_4) L_0(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4; \zeta_l). \quad (4.34)$$

Since the quasiparticle Green's function is diagonal in this particular orbital basis set, the matrix element defined above becomes

$$L_0 \frac{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_3}{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_4}(\zeta_l) = \frac{1}{\beta} \sum_{l'} \frac{1}{\hbar(z_{l'} + \zeta_l) - E_{\tilde{\mathbf{k}}_1}^{\text{qp}}} \delta_{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_4} \frac{1}{\hbar z_{l'} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}}} \delta_{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_3}. \quad (4.35)$$

The summation over the fermionic frequency, however, can be resolved using the relation

$$\frac{1}{\hbar\beta} \sum_l \frac{1}{z_l - \omega} = f(\hbar\omega) - \frac{1}{2}, \quad (4.36)$$

with the Fermi function $f(\hbar\omega)$ and its property to remain unchanged if it is shifted by a bosonic Matsubara frequency ζ_l , i.e. $f(\hbar\omega + \hbar\zeta_l) = f(\hbar\omega)$ [44]. To benefit from Eq.(4.36), the product on the rhs of Eq.(4.35) can be formulated alternatively in terms of a partial fraction decomposition that results in the expression

$$\frac{\delta_{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_4} \delta_{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_3}}{-\hbar\zeta_l + E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}}} \sum_{l'} \left\{ \frac{1}{\hbar(z_{l'} + \zeta_l) - E_{\tilde{\mathbf{k}}_1}^{\text{qp}}} - \frac{1}{\hbar z_{l'} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}}} \right\} \frac{1}{\beta}. \quad (4.37)$$

As a result one immediately finds

$$L_0 \frac{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_3}{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_4}(\zeta_l) = \frac{f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}})}{E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}} - \hbar\zeta_l} \delta_{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_4} \delta_{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_3}. \quad (4.38)$$

Hence, the resulting expression for the four-point density correlation function at the bosonic frequency ζ_l can be summarized as

$$L_0(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4; \zeta_l) = \sum_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2} \varphi_{\tilde{\mathbf{k}}_1}(\mathbf{r}_1) \varphi_{\tilde{\mathbf{k}}_2}^*(\mathbf{r}_3) \varphi_{\tilde{\mathbf{k}}_2}(\mathbf{r}_2) \varphi_{\tilde{\mathbf{k}}_1}^*(\mathbf{r}_4) \frac{f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_2}^{\text{qp}})}{E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_2}^{\text{qp}} - \hbar\zeta_l}. \quad (4.39)$$

The transition to the zero temperature limit, i.e. $T \rightarrow 0$, can be performed in Eq.(4.39), noticing that the fermi function becomes the theta function as shown below

$$\lim_{T \rightarrow 0} f(\hbar\omega) = \Theta(\mu - \hbar\omega). \quad (4.40)$$

Additionally, $L_0(\zeta_l)$ at the bosonic frequency ζ_l can be transferred to the whole imaginary complex plane in analogy with the procedure of the Green's function w.r.t. to the fermionic frequency z_l . This allows to express the independent particle approximation of the density correlation function in terms of real frequencies ω . Thus one finds in analogy with $\chi_0(1, 2)$ the time ordered expression of L_0

$$\begin{aligned} L_0(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4; \omega) = \sum_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2} \varphi_{\tilde{\mathbf{k}}_1}(\mathbf{r}_1) \varphi_{\tilde{\mathbf{k}}_2}^*(\mathbf{r}_3) \varphi_{\tilde{\mathbf{k}}_2}(\mathbf{r}_2) \varphi_{\tilde{\mathbf{k}}_1}^*(\mathbf{r}_4) \\ \times \left[\frac{\Theta(E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - \mu) \Theta(\mu - E_{\tilde{\mathbf{k}}_2}^{\text{qp}})}{\hbar\omega + E_{\tilde{\mathbf{k}}_2}^{\text{qp}} - E_{\tilde{\mathbf{k}}_1}^{\text{qp}} + i\hbar\eta} - \frac{\Theta(\mu - E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) \Theta(E_{\tilde{\mathbf{k}}_2}^{\text{qp}} - \mu)}{\hbar\omega + E_{\tilde{\mathbf{k}}_2}^{\text{qp}} - E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - i\hbar\eta} \right]. \end{aligned} \quad (4.41)$$

Obviously, the contraction of the spatial arguments, i.e. $\mathbf{r}_4 \rightarrow \mathbf{r}_2$ and $\mathbf{r}_3 \rightarrow \mathbf{r}_1$ can be performed, thus obtaining the independent quasiparticle approximation of the two-point density correlation function $\chi_0^{\text{IQPA}}(\mathbf{r}_1, \mathbf{r}_2; \omega) = L_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2; \omega)$. The comparison of the resulting expression for χ_0^{IQPA} with that of χ_0 immediately shows that the transition from the independent particle approximation to the corresponding independent quasiparticle approximation goes along with the substitution $\varepsilon_{\tilde{\mathbf{k}}} \rightarrow E_{\tilde{\mathbf{k}}}^{\text{qp}}$ of the corresponding term in the frequency domain. Evenmore, we find the retarded microscopic dielectric function in analogy with the derivation within the independent particle approximation and can simply adopt the result that leads to

$$\epsilon_{\mathbf{G}\mathbf{G}'}^{\text{IQPA}}(\mathbf{q}; \omega) = \delta_{\mathbf{G}\mathbf{G}'} - \frac{4\pi e^2}{|\mathbf{q} + \mathbf{G}|^2} \sum_{\tilde{\mathbf{k}}_1, \tilde{\mathbf{k}}_2} B_{\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1*}(\mathbf{q} + \mathbf{G}) B_{\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1}(\mathbf{q} + \mathbf{G}') \frac{\Theta(\mu - E_{\tilde{\mathbf{k}}_2}^{\text{qp}}) - \Theta(\mu - E_{\tilde{\mathbf{k}}_1}^{\text{qp}})}{\hbar\omega + E_{\tilde{\mathbf{k}}_2}^{\text{qp}} - E_{\tilde{\mathbf{k}}_1}^{\text{qp}} + i\hbar\eta}. \quad (4.42)$$

4.1.7. Excitonic Hamiltonian ⁸

So far, we have examined the solution of the independent (quasi)-particle approximation for the microscopic dielectric function $\epsilon(\omega)$. In order to include excitonic effects due to the electron-hole coupling, we have to solve the full Bethe-Salpeter equation for the density correlation function L . Although, the inverse dielectric function is a two-point quantity as given by Eq.(3.116), the density correlation function $L(12)$ does not obey a Bethe-Salpeter equation due to the coupling kernel Ξ' . Just in the case if the non-local screened interaction is neglected, i.e. $\Xi = 0$ the resulting BSE for $L(1, 3, 2, 4)$ turns into a closed Dyson equation for the two-point density correlation function $L(12)$. This approximation is also known as the random phase approximation for the

⁷One may note that the inverse microscopic dielectric function is related to the density correlation function L . Within the independent (quasi)-particle approximation we have $L^{\text{I(Q)P}} = P^{\text{I(Q)P}}$. Therefore it is equivalent to solve the dielectric function from $\epsilon_{\mathbf{G}\mathbf{G}'}^{\text{I(Q)P}}(\mathbf{q}) = \delta_{\mathbf{G}\mathbf{G}'} - v_{\mathbf{G}}(\mathbf{q}) P_{\mathbf{G}\mathbf{G}'}^{\text{I(Q)P}}(\mathbf{q})$. It can be shown with the aid of the Sherman-Morrison formula that by inversion of the matrix $\epsilon_{\mathbf{G}\mathbf{G}'}^{-1 \text{I(Q)P}}(\mathbf{q}) = \delta_{\mathbf{G}\mathbf{G}'} + v_{\mathbf{G}}(\mathbf{q}) P_{\mathbf{G}\mathbf{G}'}^{\text{I(Q)P}}(\mathbf{q})$ one obtains exactly the expression for $\epsilon_{\mathbf{G}\mathbf{G}'}^{\text{I(Q)P}}(\mathbf{q})$.

⁸I follow partially Refs. [44, 49].

density correlation function denoted by L^{RPA} . However, in order to obtain the full solution for $L(1, 3, 2, 4)$ we can exploit the Bloch representation as discussed in the previous section also for L as it is a functional of L_0 . Hence, substituting Eq.(4.33) into the BSE [Eq.(3.136)] for L and taking the limes $t_4 \rightarrow t_{2+}$, one eventually finds by comparison of the coefficients the following relation

$$\begin{aligned} L_{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_3}(t_1 - t_3, t_1 - t_2) = & -i\hbar G_{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_4}(t_1 - t_{2+}) G_{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_3}(t_2 - t_3) \\ & + i\hbar \sum_{\substack{\tilde{\mathbf{k}}'_5, \tilde{\mathbf{k}}'_6 \\ \tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8}} \left[G_{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}'_5}(t_1 - t_6) G_{\tilde{\mathbf{k}}'_6 \tilde{\mathbf{k}}_3}(t_6 - t_3) v_{\tilde{\mathbf{k}}'_8 \tilde{\mathbf{k}}'_7}^{\tilde{\mathbf{k}}'_5 \tilde{\mathbf{k}}'_6} L_{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7 \tilde{\mathbf{k}}'_8}(t_6 - t_6, t_6 - t_2) \right. \\ & \left. - i\hbar \iint dt_7 dt_8 G_{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}'_5}(t_1 - t_7) G_{\tilde{\mathbf{k}}'_6 \tilde{\mathbf{k}}_3}(t_8 - t_3) W_{\tilde{\mathbf{k}}'_8 \tilde{\mathbf{k}}'_7}^{\tilde{\mathbf{k}}'_5 \tilde{\mathbf{k}}'_6}(t_7 - t_8) L_{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7 \tilde{\mathbf{k}}'_8}(t_7 - t_8, t_7 - t_2) \right]. \end{aligned} \quad (4.43)$$

In particular, the matrix elements for the Coulomb term and the screened interaction read in position space

$$\begin{aligned} v_{\tilde{\mathbf{k}}'_8 \tilde{\mathbf{k}}'_7}^{\tilde{\mathbf{k}}'_5 \tilde{\mathbf{k}}'_6} = & \iiint \int d\mathbf{r}_5 d\mathbf{r}_6 d\mathbf{r}_7 d\mathbf{r}_8 \varphi_{\tilde{\mathbf{k}}'_5}^*(\mathbf{r}_5) \varphi_{\tilde{\mathbf{k}}'_6}(\mathbf{r}_6) \delta(\mathbf{r}_5 - \mathbf{r}_6) \delta(\mathbf{r}_7 - \mathbf{r}_8) v(\mathbf{r}_5 - \mathbf{r}_8) \varphi_{\tilde{\mathbf{k}}'_8}^*(\mathbf{r}_8) \varphi_{\tilde{\mathbf{k}}'_7}(\mathbf{r}_7) \\ = & \iint d\mathbf{r}_6 d\mathbf{r}_8 \varphi_{\tilde{\mathbf{k}}'_5}^*(\mathbf{r}_6) \varphi_{\tilde{\mathbf{k}}'_6}(\mathbf{r}_6) v(\mathbf{r}_6 - \mathbf{r}_8) \varphi_{\tilde{\mathbf{k}}'_8}^*(\mathbf{r}_8) \varphi_{\tilde{\mathbf{k}}'_7}(\mathbf{r}_8) \end{aligned} \quad (4.44)$$

and

$$\begin{aligned} W_{\tilde{\mathbf{k}}'_8 \tilde{\mathbf{k}}'_7}^{\tilde{\mathbf{k}}'_5 \tilde{\mathbf{k}}'_6} = & \iiint \int d\mathbf{r}_5 d\mathbf{r}_6 d\mathbf{r}_7 d\mathbf{r}_8 \varphi_{\tilde{\mathbf{k}}'_5}^*(\mathbf{r}_5) \varphi_{\tilde{\mathbf{k}}'_6}(\mathbf{r}_6) \delta(\mathbf{r}_5 - \mathbf{r}_7) \delta(\mathbf{r}_6 - \mathbf{r}_8) W(\mathbf{r}_5, \mathbf{r}_6) \varphi_{\tilde{\mathbf{k}}'_8}^*(\mathbf{r}_8) \varphi_{\tilde{\mathbf{k}}'_7}(\mathbf{r}_7) \\ = & \iint d\mathbf{r}_7 d\mathbf{r}_8 \varphi_{\tilde{\mathbf{k}}'_5}^*(\mathbf{r}_7) \varphi_{\tilde{\mathbf{k}}'_6}(\mathbf{r}_8) W(\mathbf{r}_7, \mathbf{r}_8) \varphi_{\tilde{\mathbf{k}}'_8}^*(\mathbf{r}_8) \varphi_{\tilde{\mathbf{k}}'_7}(\mathbf{r}_7) \end{aligned} \quad (4.45)$$

Equation (4.43) reveals that as long as the density-correlation function depends on two time arguments, the GW -approximation of the BSE for L does not yield a closed equation in terms of the time arguments and eventually also in terms of the frequency arguments. As we are interested in a one-frequency dependent density-correlation function $L(\zeta_l)$, which then can be related to the one-frequency dependent dielectric function, the limes $t_3 \rightarrow t_{1+}$ in Eq.(4.43) can be performed without loss of generality. However, due to the dynamic screened interaction, the resulting equation for L still requires the solution of a two-time dependent density correlation function. This can be done for instance in an approximative manner exploiting the Shindo-approximation [86, 85]. The inclusion of such dynamical effects, however, does not give rise to an improved description of the excitonic effects in determining optical properties. This is mainly due to a compensation of dynamical quasiparticle effects and dynamical vertex corrections [87]. Therefore, one usually sticks to the static approximation of the screened interaction, i.e. $W(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \approx W(\mathbf{r}_1, \mathbf{r}_2) \delta(t_1 - t_2)$. Obviously, this affects Eq.(4.43) and turns it into a closed equation with a density correlation function that depends only on one time argument $t_1 - t_2$ and

can thus be transformed to a one-frequency dependent quantity within the frequency domain:

$$\begin{aligned}
L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}(\zeta_l) = & \frac{1}{\beta} \sum_{l'} \left[G_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_4}(z_{l'} + \zeta_l) G_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_3}(z_{l'}) \right. \\
& + \sum_{\tilde{\mathbf{k}}'_5, \tilde{\mathbf{k}}'_6, \tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} G_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}'_5}(z_{l'} + \zeta_l) G_{\tilde{\mathbf{k}}'_6\tilde{\mathbf{k}}_3}(z_{l'}) v_{\tilde{\mathbf{k}}'_5\tilde{\mathbf{k}}'_6} L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l) \\
& \left. - \sum_{\tilde{\mathbf{k}}'_5, \tilde{\mathbf{k}}'_6, \tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} G_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}'_5}(z_{l'} + \zeta_l) G_{\tilde{\mathbf{k}}'_6\tilde{\mathbf{k}}_3}(z_{l'}) W_{\tilde{\mathbf{k}}'_5\tilde{\mathbf{k}}'_6}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8} L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l) \right]. \quad (4.46)
\end{aligned}$$

Again, the summation over the fermionic Matsubara frequencies can be performed by use of Eq.(4.38) and the corresponding diagonal matrix element of the quasiparticle Green's function [Eq.(3.87)]

$$L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}(\zeta_l) = \frac{f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}})}{E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}} - \hbar\zeta_l} \left\{ \delta_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_4} \delta_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_3} + \sum_{\tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} \left[v_{\tilde{\mathbf{k}}'_8\tilde{\mathbf{k}}'_7} - W_{\tilde{\mathbf{k}}'_8\tilde{\mathbf{k}}'_7} \right] L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l) \right\}. \quad (4.47)$$

With Eq.(4.47) the Bethe-Salpeter equation for the density-correlation function has been transformed to a matrix form in terms of pairs of Bloch orbitals, i.e. $(\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3)$ and $(\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4)$. These pairs obviously appear in combination of occupied and unoccupied pairs as it is clearly seen from the difference of the Fermi function in Eq.(4.47) for the upper pair of Bloch orbitals. However, also the second lower pair of the matrix element $L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}$ yields contributions for L in the combination of occupied and unoccupied Bloch orbitals. This can be deduced from the Bethe-Salpeter equation for L [Eq.(3.124)], which explicitly can be written like $L = L_0 + L_0[v - W]L_0 + \dots$. The full solution of the matrix $L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}(\zeta_l)$ can be obtained by matrix inversion. For that one introduces the excitonic Hamilton operator H , which is given within the basis of Bloch orbitals as

$$H_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} = \left(E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}} \right) \mathbb{1}_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} - \left[f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \right] I_{\tilde{\mathbf{k}}_4\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}, \quad (4.48)$$

while the interaction kernel I abbreviates the difference of the Coulomb term and the screened interaction term from Eq.(4.47), i.e. $I = v - W$. It allows, as shown in the appendix I, to write a matrix equation for the density correlation function as

$$f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \mathbb{1}_{\tilde{\mathbf{k}}_4\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} = \sum_{\tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} \left[H_{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} - \hbar\zeta_l \mathbb{1}_{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} \right] L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l). \quad (4.49)$$

The inversion of the matrix $[H - \hbar\zeta_l \mathbb{1}]$ leads to the desired matrix for L . One may note, however, that by inspection of Eq.(4.49) the matrix on the rhs differs in the lower index pair compared to the unity matrix on the lhs. The previously introduced indexing $\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4$ stems from Eq.(4.33) and can, without loss of generality, be interchanged to $\tilde{\mathbf{k}}_4\tilde{\mathbf{k}}_2$. By doing so, the lower index of L in Eq.(4.49) can be swapped so that Eq.(4.49) displays a valid matrix equation given by the general matrix product $C_{cd}^{ab} = \sum_{e,f} A_{ef}^{ab} B_{cd}^{ef}$ [49].

Structure of the excitonic Hamiltonian

As mentioned above, the matrix elements of the density correlation function $L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}$ are restricted to pairs of occupied and unoccupied Bloch orbitals. Since these matrix elements enters into the calculation of the (inverse) microscopic dielectric function $\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q})$ the index pairs are explicitly given as

$$(\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3) = (c\mathbf{k}, v\mathbf{k} + \mathbf{q}), (v\mathbf{k}, c\mathbf{k} + \mathbf{q}) \quad \text{and} \quad (\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4) = (c'\mathbf{k}', v'\mathbf{k}' + \mathbf{q}), (v'\mathbf{k}', c'\mathbf{k}' + \mathbf{q}) \quad (4.50)$$

or within the optical limes $\mathbf{q} \rightarrow 0$ where only vertical transitions are considered

$$(\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3) = (cv, \mathbf{k}), (vc, \mathbf{k}) \quad \text{and} \quad (c'v', \mathbf{k}'), (v'c', \mathbf{k}'). \quad (4.51)$$

For the latter case the excitonic Hamiltonian given in Eq.(4.48) has the following structure

$$H_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} = \left(\begin{array}{c|cc} \begin{array}{l} \downarrow (\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3) \\ \rightarrow (\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4) \end{array} & c'v'\mathbf{k}' & v'c'\mathbf{k}' \\ \hline cv\mathbf{k} & {}^r H_{c'v'\mathbf{k}'}^{cv\mathbf{k}} & I_{c'v'\mathbf{k}'}^{cv\mathbf{k}} \\ \hline vc\mathbf{k} & -[I_{c'v'\mathbf{k}'}^{cv\mathbf{k}}]^* & {}^a H_{v'c'\mathbf{k}'}^{vc\mathbf{k}} \end{array} \right). \quad (4.52)$$

The upper left submatrix denotes the resonant part of H and reads explicitly

$${}^r H_{c'v'\mathbf{k}'}^{cv\mathbf{k}} = \delta_{cc'}\delta_{vv'}\delta_{\mathbf{k}\mathbf{k}'} (E_{c\mathbf{k}}^{\text{qp}} - E_{v\mathbf{k}}^{\text{qp}}) + I_{v'c'\mathbf{k}'}^{cv\mathbf{k}}. \quad (4.53)$$

Furthermore, the matrix element of the interaction kernel I are hermitian, i.e. $I_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}^{\tilde{\mathbf{k}}_4\tilde{\mathbf{k}}_2} = [I_{\tilde{\mathbf{k}}_4\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}]^*$, because the Coulomb kernel $v(|\mathbf{r}_1 - \mathbf{r}_2|)$ as well as the static screened interaction $W(\mathbf{r}_1, \mathbf{r}_2)$ are symmetric w.r.t their spatial arguments [60]. The antiresonant part of the excitonic Hamiltonian can be written as

$${}^a H_{v'c'\mathbf{k}'}^{vc\mathbf{k}} = \delta_{cc'}\delta_{vv'}\delta_{\mathbf{k}\mathbf{k}'} (E_{v\mathbf{k}}^{\text{qp}} - E_{c\mathbf{k}}^{\text{qp}}) - I_{c'v'\mathbf{k}'}^{vc\mathbf{k}} = -[{}^r H_{c'v'\mathbf{k}'}^{cv\mathbf{k}}]^*. \quad (4.54)$$

Finally, the matrix representation of L , as given in Eq.(4.49), is obtained from the solution of the matrix $[\bar{H} - \hbar\zeta_l\bar{\mathbb{I}}]^{-1}$. This can be achieved by the resolvent of the excitonic operator H . Therefore, one has to solve the corresponding eigenvalue problem of H , i.e.

$$H|\Upsilon_\Lambda\rangle = E_\Lambda|\Upsilon_\Lambda\rangle \quad \text{or} \quad \sum_{(n_2n_4\mathbf{k}_2)} H_{n_2n_4\mathbf{k}_2}^{n_1n_3\mathbf{k}_1} \Upsilon_\Lambda^{n_2n_4\mathbf{k}_2} = E_\Lambda^{n_1n_3\mathbf{k}_1} \Upsilon_\Lambda^{n_1n_3\mathbf{k}_1}. \quad (4.55)$$

The bosonic problem of solving the matrix $[\bar{H} - \hbar\zeta_l\bar{\mathbb{I}}]^{-1}$ hence reduces to the familiar problem of solving the Green's function operator $\mathcal{G}$ that obeys the equation $[H - \hbar\zeta_l]\mathcal{G} = \mathbb{1}$ or equivalently $\mathcal{G} = \frac{1}{[H - \hbar\zeta_l]}$. With the aid of the closure relation, the Green's operator can be expressed in terms

⁹The summation over the indices n_2, n_4 runs over all bands with the condition $n_2 = c \leftrightarrow n_4 = v$ and vice versa.

of the eigenvectors Υ_Λ and yields the resolvent representation of H ¹⁰:

$$\begin{aligned}
\mathcal{G} &= \sum_{\Lambda, \Lambda'} |\Upsilon_\Lambda\rangle \langle \Upsilon_\Lambda| \frac{1}{[H - \hbar\zeta_l]} |\Upsilon'_{\Lambda'}\rangle \langle \Upsilon'_{\Lambda'}| \\
&= \sum_{\Lambda, \Lambda'} |\Upsilon_\Lambda\rangle \langle \Upsilon_\Lambda| \frac{-1}{\hbar\zeta_l \left(1 - \frac{H}{\hbar\zeta_l}\right)} |\Upsilon'_{\Lambda'}\rangle \langle \Upsilon'_{\Lambda'}| \\
&= \sum_{\Lambda, \Lambda'} |\Upsilon_\Lambda\rangle \langle \Upsilon_\Lambda| \frac{-1}{\hbar\zeta_l \left(1 - \frac{E_\Lambda}{\hbar\zeta_l}\right)} |\Upsilon'_{\Lambda'}\rangle \langle \Upsilon'_{\Lambda'}| \\
&= \sum_{\Lambda, \Lambda'} \frac{|\Upsilon_\Lambda\rangle \langle \Upsilon'_{\Lambda'}|}{E_\Lambda - \hbar\zeta_l} \delta_{\Lambda, \Lambda'}.
\end{aligned} \tag{4.56}$$

The derivation above requires, however, some explanation. First of all, the matrix $\bar{H}$ is, by its full representation as displayed in Eq.(4.52), not hermitian, although its submatrices are hermitian. Under the assumption of the resonant part ${}^r\bar{H}$ being positiv definite, one may show that H has only real eigenvalues E_Λ [60, 49]. Secondly, the matrix $\bar{H}$ has, as it is not hermitian, a set of left $\{|\Upsilon_\Lambda\rangle\}$ and right eigenvectors $\{|\Upsilon'_{\Lambda'}\rangle\}$ that are additionally bi-orthogonal, i.e. $\langle \Upsilon_\Lambda | \Upsilon'_{\Lambda'} \rangle = \delta_{\Lambda, \Lambda'}$ and have eigenvalues E_Λ and E_Λ^* , respectively [88] and leads to the representation of the Green's operator in Eq.(4.56). Hence, Eq.(4.49) can now be inverted to obtain the density correlation function in terms of the Bloch basis as the following

$$L_{\tilde{\mathbf{k}}_2 \tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1 \tilde{\mathbf{k}}_3}(\zeta_l) = \left[f(E_{n_1 \mathbf{k}_1}^{\text{qp}}) - f(E_{n_3 \mathbf{k}_1}^{\text{qp}}) \right] \sum_{\Lambda} \frac{\Upsilon_{\Lambda}^{n_1 n_3 \mathbf{k}_1} \Upsilon_{\Lambda}^{\prime n_2 n_4 \mathbf{k}_2 *}}{E_{\Lambda} - \hbar\zeta_l}. \tag{4.57}$$

Even though the density correlation function has to be evaluated for every frequency ζ_l , the resolvent representation due to Eq.(4.57) circumvents to evaluate the inverse matrix $[\bar{H} - \hbar\zeta_l \mathbb{I}]^{-1}$ for every frequency. Nevertheless, the corresponding eigenvalue problem for the excitonic Hamiltonian [Eq.(4.55)] is indispensable in order to include the excitonic effects for the calculation of the microscopic dielectric function. It is therefore the main numerically demanding task and thus limits the inclusion of the number of pairs of conduction/valence-bands in practical applications. In particular, the neglect of the off-diagonal submatrices in Eq.(4.52), i.e. the couplings terms $I_{c'v'\mathbf{k}'}^{cv\mathbf{k}}$, decomposes the excitonic Hamiltonian to the sum of the resonant and antiresonant submatrices. Additionally, the resonant part rH is related to the antiresonant part, simply by its conjugation and thus it is sufficient to solve the resulting hermitian eigenvalue problem for rH only. The corresponding eigenvectors of the antiresonant submatrix aH are then obtained from the eigenvectors corresponding to the solution of the EVP of rH . Hence one finds

$${}^a\Upsilon_{\Lambda}^{v\mathbf{k}*} = {}^r\Upsilon_{\Lambda}^{cv\mathbf{k}} \quad \text{and} \quad {}^rE_{\Lambda} = -{}^aE_{\Lambda}. \tag{4.58}$$

This approximation is known as the *Tamm-Dancoff approximation (TDA)*[89, 90] and gives reasonable results for semiconducting materials[91, 92, 93], as in these materials the inclusion of the coupling terms $I_{c'v'\mathbf{k}'}^{cv\mathbf{k}}$ do not yield improved optical spectra. Furthermore, the application

¹⁰We use in the following derivation the series expansion $\frac{1}{1-x} = 1 + x + x^2 + \dots$

of the full excitonic Hamiltonian to extended systems requires a transformation to a Hermitian expression and is one part of the main work of this thesis. Additionally, it has been shown that the inclusion of the off-diagonal matrices yields to different optical spectra for systems with distinctive electronic density inhomogeneities [94].

4.1.8. Macroscopic dielectric function - beyond the independent quasiparticle approximation (TDA)

Within the Tamm-Dancoff approximation, the density correlation function L , if expressed in the Bloch basis, can be eventually expressed by a full resonant part and a full antiresonant part. With the definition given by Eq.(4.33) and the inclusion of only vertical transition pairs, one finds

$$\begin{aligned}
 L^{\text{TDA}}(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2, \mathbf{r}_4 | \zeta_l) = & \\
 & \sum_{\substack{c,v,\mathbf{k} \\ c',v',\mathbf{k}'}} \varphi_{c\mathbf{k}}(\mathbf{r}_1) \varphi_{v\mathbf{k}}^*(\mathbf{r}_3) \varphi_{c'\mathbf{k}'}(\mathbf{r}_2) \varphi_{v'\mathbf{k}'}^*(\mathbf{r}_4) \left[- \sum_{\Lambda} \frac{\Upsilon_{\Lambda}^{cv\mathbf{k}} \Upsilon_{\Lambda}^{c'v'\mathbf{k}'*}}{E_{\Lambda} - \hbar\zeta_l} \right] \\
 & + \sum_{\substack{c,v,\mathbf{k} \\ c',v',\mathbf{k}'}} \varphi_{v\mathbf{k}}(\mathbf{r}_1) \varphi_{c\mathbf{k}}^*(\mathbf{r}_3) \varphi_{v'\mathbf{k}'}(\mathbf{r}_2) \varphi_{c'\mathbf{k}'}^*(\mathbf{r}_4) \left[\sum_{\Lambda} \frac{\Upsilon_{\Lambda}^{v\mathbf{k}} \Upsilon_{\Lambda}^{v'c'\mathbf{k}'*}}{-E_{\Lambda} - \hbar\zeta_l} \right].
 \end{aligned} \tag{4.59}$$

Similar to the case for the independent (quasi)-particle approximation, we can take the limes w.r.t the spatial coordinates, i.e. $\mathbf{r}_3 \rightarrow \mathbf{r}_1$ and $\mathbf{r}_4 \rightarrow \mathbf{r}_2$ to obtain the inverse microscopic dielectric function in the reciprocal space. As we already imply the long wave length limit by considering only vertical transitions between the pairs $(cv\mathbf{k})$ and $(v\mathbf{k})$, the resulting Bloch integrals reduces to the components $B_{v\mathbf{k}}^{c\mathbf{k}}(\mathbf{q})$ and we obtain the intermediate result for the inverse dielectric function in the reciprocal space:

$$\epsilon_{\mathbf{G}=0\mathbf{G}'=0}^{-1}(\mathbf{q}) = 1 + \frac{4\pi e^2}{|\mathbf{q}|^2} \sum_{\substack{\Lambda \\ c,v,\mathbf{k} \\ c',v',\mathbf{k}'}} B_{v\mathbf{k}}^{c\mathbf{k}*}(\mathbf{q}) B_{v'\mathbf{k}'}^{c'\mathbf{k}'}(\mathbf{q}) \Upsilon^{(cv\mathbf{k})} \Upsilon^{(c'v'\mathbf{k}')*} \left[\frac{-1}{E_{\Lambda} - \hbar\zeta_l} + \frac{-1}{E_{\Lambda} + \hbar\zeta_l} \right] \tag{4.60}$$

In principle, Eq.(4.60) is exact but needs to be treated carefully, if the limes $\mathbf{q} \rightarrow 0$ is considered. First of all, this equation can also be written as $\epsilon_{00}^{-1}(\mathbf{q}) = 1 + v(\mathbf{q}) L_{00}^{\text{TDA}}(\mathbf{q})$, with the reciprocal Fourier coefficient $L_{\mathbf{G}\mathbf{G}'}^{\text{TDA}}(\mathbf{q})$ obtained from Eq.(3.120) given in Fourier space

$$L_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) + \sum_{\tilde{\mathbf{G}}} P_{\mathbf{G}\tilde{\mathbf{G}}}(\mathbf{q}) v_{\tilde{\mathbf{G}}}(\mathbf{q}) L_{\tilde{\mathbf{G}}\mathbf{G}'}(\mathbf{q}) \tag{4.61}$$

and taken at reciprocal lattice vectors $\mathbf{G} = \mathbf{G}' = 0$. Obviously, there are two diverging terms, the Coulomb kernel in Eq.(4.60) and the Coulomb kernel in Eq.(4.61) that seemingly appears in the interaction kernel I . In principle, in gapped systems the $\frac{1}{|\mathbf{q}|^2}$ divergence in Eq.(4.60) is cancelled due to the matrix elements $B_{v\mathbf{k}}^{c\mathbf{k}}(\mathbf{q})$ decaying like $\mathbf{q}$. However, this requires carefully coding, and in non-cubic materials results also depend on how the limes $\mathbf{q} \rightarrow 0$ is approached.

About the divergence due to the Coulomb kernel in I , it can be shown that by a substitution of the original kernel $v_{\mathbf{G}}(\mathbf{q})$ through an amputated kernel $\bar{v}_{\mathbf{G}}(\mathbf{q})$

$$\bar{v}_{\mathbf{G}}(\mathbf{q}) = \begin{cases} 0 & \text{if } \mathbf{G} = 0 \\ v_{\mathbf{G}}(\mathbf{q}) & \text{if } \mathbf{G} \neq 0, \end{cases} \quad (4.62)$$

the limes in Eq.(4.60) can be safely performed if Eq.(4.60) is evaluated with the amputated density correlation function $\bar{L} \equiv L_0 + L_0(\bar{v} - W)L$. Evenmore, the macroscopic limit of L is then given by $\bar{L}_{00}(\mathbf{q})$ and the macroscopic dielectric function is given as [62]

$$\epsilon_{\text{M}}(\hat{\mathbf{q}}|\zeta_l) = 1 - \lim_{\mathbf{q} \rightarrow 0} [v_0(\mathbf{q})\bar{L}_{00}(\mathbf{q}|\zeta_l)]. \quad (4.63)$$

Taking this modifications into account, the rhs of Eq.(4.60) immediately leads to the macroscopic dielectric function $\epsilon_{\text{M}}(\hat{\mathbf{q}})$ within the TDA

$$\epsilon_{\text{M}}^{\text{TDA}}(\hat{\mathbf{q}}|\zeta_l) = 1 + 4\pi e^2 \sum_{\substack{\Lambda \\ c,v,\mathbf{k}}} \left| M_{v\mathbf{k}}^{c\mathbf{k}*}(\hat{\mathbf{q}}) \tilde{\Upsilon}_{\Lambda}^{(cv\mathbf{k})} \right|^2 \left[\frac{1}{E_{\Lambda} - \hbar\zeta_l} + \frac{1}{E_{\Lambda} + \hbar\zeta_l} \right].^{11} \quad (4.64)$$

Eventually, the transition from the complex frequency $\zeta_l \rightarrow \omega + i\eta$ allows to access the retarded dielectric function. To summarize, Eq.(4.60) is not the appropriate equation that can be used to obtain the macroscopic limit of the dielectric function as it contains a divergent Coulomb kernel in the reciprocal space. However, the simple modification by substituting the Coulomb kernel with its amputated counterpart yields the possibility to solve the macroscopic dielectric function immediately from equation 4.63. I will give evidence in section 4.1.10.

4.1.9. Microscopic and macroscopic relations

In this section I want to shortly demonstrate the relation between the microscopic and macroscopic description of the involved response quantities. Within the linear response theory we are interested in the response of the underlying many-particle system due to a small external perturbation. The latter one is usually taken as potential V_{ext} associated to an external charge distribution that causes a response of the system building up a screened potential V_{tot} . It is related to the external potential by the inverse microscopic dielectric function

$$V_{\text{tot}}(\mathbf{r}, t) = \int d\mathbf{r}' dt' \epsilon^{-1}(\mathbf{r}, \mathbf{r}'; t - t') V_{\text{ext}}(\mathbf{r}', t') \quad (4.65)$$

or equivalently in Fourier space

$$V_{\mathbf{G}}^{\text{tot}}(\mathbf{q}, \omega) = \sum_{\mathbf{G}'} \epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}, \omega) V_{\mathbf{G}'}^{\text{ext}}(\mathbf{q}, \omega). \quad (4.66)$$

¹¹We want to distinguish between the eigenvectors Υ_{Λ} corresponding to the original excitonic Hamiltonian and those, i.e. $\tilde{\Upsilon}_{\Lambda}$, that are eigenvectors of H with the amputated Coulomb kernel $\bar{v}$.

Since the dielectric function, as well as the total potential are conform with the lattice symmetry, the vector $\mathbf{q}$ belongs to the first Brillouin zone, while the vectors $\mathbf{G}$ and $\mathbf{G}'$ are reciprocal lattice vectors. As the external potential will have a macroscopic characteristic it will consist of a main Fourier component associated to a wave length large against the microscopic structure, but still small enough compared to the length of the sample. The microscopic field in the crystal are responsible for the so-called local field and are accounted by the non-local form of the dielectric function. Hence, the macroscopic perturbation given by $V_{\mathbf{G}}^{\text{ext}}\delta_{0,\mathbf{G}}$ still lead to a modification of the local fields that contributes to the total potential. In particular, in many-particle system with a strongly varying electron density, the local field effects play a crucial role when the dielectric properties are of interest and thus cannot be neglected. Eq.(4.65) as well Eq.(4.66) represent the microscopic equations. Since for practical applications only macroscopic quantities are accessible, the microscopic potential undergoes an average procedure, i.e. one calculates the corresponding potential averaged over a unit cell with volume V_0 and with origin at point $\mathbf{R}$. One thus obtains

$$V_{\text{tot},M}(\mathbf{R}, \omega) = \langle V^{\text{tot}}(\mathbf{r}, \omega) \rangle_{\mathbf{R}} = \frac{1}{V_0} \int_{V_0(\mathbf{R})} d\mathbf{r}' V_{\text{tot}}(\mathbf{r}', \omega). \quad (4.67)$$

Decomposing the total potential in Fourier components, i.e.

$$V_{\text{tot}}(\mathbf{r}, \omega) = \sum_{\mathbf{G}} V_{\mathbf{G}}^{\text{tot}}(\mathbf{q}, \omega) e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} \quad (4.68)$$

and substitute Eq.(4.68) in Eq.(4.67) one obtains

$$V_{\text{tot},M}(\mathbf{R}, \omega) = \frac{1}{V_0} \sum_{\mathbf{G}} V_{\mathbf{G}}^{\text{tot}}(\mathbf{q}, \omega) \int_{V_0(\mathbf{R})} d\mathbf{r}' e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}'}. \quad (4.69)$$

The equation above can be further simplified by taking the exponential $e^{i\mathbf{q}\mathbf{r}'}$ in front of the integral because the wave vector $\mathbf{q}$ associated to the external potential varies only slowly over the unit cell and can be treated as a constant [95]. Thus one finds

$$V_{\text{tot},M}(\mathbf{R}, \omega) = \frac{1}{V_0} \sum_{\mathbf{G}} V_{\mathbf{G}}^{\text{tot}}(\mathbf{q}, \omega) e^{i\mathbf{q}\mathbf{R}} \int_{V_0(\mathbf{R})} d\mathbf{r}' e^{i\mathbf{G}\mathbf{r}'} \quad (4.70)$$

The integral in Eq.(4.70) contributes only for a vanishing reciprocal lattice vector and yields $V_0 \delta_{0,\mathbf{G}}$. As a consequence, the Fourier coefficient $V_{\mathbf{G}}^{\text{tot}}(\mathbf{q}, \omega)\delta_{0,\mathbf{G}}$ of the microscopic potential is equivalent to the Fourier coefficient of the corresponding macroscopic potential, i.e.

$$V_{\mathbf{G},M}^{\text{tot}}(\mathbf{q}, \omega) = V_{\mathbf{G}}^{\text{tot}}(\mathbf{q}, \omega)\delta_{0,\mathbf{G}}. \quad (4.71)$$

With this result, the relation between the macroscopic total potential and a macroscopic external potential can be set up from Eq.(4.66) as

$$V_{\mathbf{G},\mathbf{M}}^{\text{tot}}(\mathbf{q},\omega)\delta_{0\mathbf{G}} = \sum_{\mathbf{G}'} \epsilon_{00}^{-1}(\mathbf{q},\omega) V_{\mathbf{G}'}^{\text{ext}}(\mathbf{q},\omega) \delta_{0,\mathbf{G}'}. \quad (4.72)$$

The crucial quantity is the head of the inverse of microscopic dielectric function $\epsilon_{00}^{-1}(\mathbf{q},\omega)$ that obviously relates both macroscopic potentials, i.e. $V_{\mathbf{M}}^{\text{tot}}$ and V^{ext} to each other. Following Eq.(4.66), it can be considered as the inverse of the macroscopic dielectric function $\epsilon_{\mathbf{M}}^{-1}$:

$$\epsilon_{\mathbf{M}}^{-1}(\mathbf{q},\omega) = \epsilon_{00}^{-1}(\mathbf{q},\omega) \leftrightarrow \epsilon_{\mathbf{M}}(\mathbf{q},\omega) = \frac{1}{\epsilon_{00}^{-1}(\mathbf{q},\omega)} \equiv \frac{1}{\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q},\omega)|_{\mathbf{G}=\mathbf{G}'=0}} \quad (4.73)$$

In other words, the macroscopic dielectric function is gained from the microscopic response function, i.e. the inverse dielectric function, taking the head of the Fourier component $\mathbf{G} = \mathbf{G}' = 0$ and finally calculating the inverse. In the case of so called homogenous materials, such as the homogenous electron gas, with a smoothly varying background potential on the microscopic scale, higher Fourier components $V_{\mathbf{G}}(\mathbf{q},\omega)$ with $\mathbf{G} \neq 0$ may be disregarded and thus local field effects are not taken into account. Under these special circumstances, the macroscopic dielectric function is then obtained by

$$\epsilon_{\mathbf{M}}^{\text{n.l.f.}}(\mathbf{q},\omega) = \epsilon_{00}(\mathbf{q},\omega). \quad (4.74)$$

The relations between the microscopic and macroscopic dielectric function have been derived independently by Adler[81] and Wiser[82] and by Ehrenreich[95].

4.1.10. Reasoning of the amputated Coulomb kernel in the BSE for L

Dyson form for L

As we have pointed out in the previous section, the macroscopic dielectric function is determined by the amputated density-correlation function $\bar{L}$ in Eq.(4.63). As this equation is the central equation that will be used to calculate $\epsilon_{\mathbf{M}}$, we want to shortly verify it and show the necessity to introduce the amputated Coulomb kernel $\bar{v}$ that leads to the corresponding BSE for $\bar{L}$. For this reason, it is important to recall the BSE for L given in the four point notation due to Eq.(3.136). It may be transformed to a Dyson-like equation that connects the irreducible part of the density-correlation function, call it $\tilde{L}$, to the reducible part, i.e. L . Considering the four point quantities in Eq.(3.136) as matrices in the spatial arguments, the same equation may be written in short form as

$$L = L_0 + L_0 (v - W) L, \quad (4.75)$$

or equivalently

$$L^{-1} = L_0^{-1} - (v - W). \quad (4.76)$$

If we define the irreducible part $\tilde{L}^{-1} = L_0^{-1} + W$, then a Dyson-like equation of the form $\tilde{L} = L_0 - L_0 W \tilde{L}$ can be deduced by analogy with Eq.(4.75). On the other, Eq.(4.76) reads with

the aid of $\tilde{L}$

$$L^{-1} = \tilde{L}^{-1} - v \quad (4.77)$$

and yields the following Dyson-like equation

$$L = \tilde{L} + \tilde{L}vL. \quad (4.78)$$

The Coulomb kernel in the equation above is given in its four-point notation, i.e. $v(1, 2, 3, 4) = \delta(1 - 2)\delta(3 - 4)v(1 - 4)$. Substituting the kernel into Eq.(4.78) one finally obtains[96, 60]

$$L(1, 3, 2, 4) = \tilde{L}(1, 3, 2, 4) + \tilde{L}(1, 3, 5, 5)v(5 - 6)L(6, 6, 2, 4). \quad (4.79)$$

One may note that by contraction of arguments, i.e. $3 \rightarrow 1$ and $4 \rightarrow 2$ in Eq.(4.79), the Dyson equation for the two-point density-correlation function $\chi(12) \equiv L(1, 2)$ [Eq.(3.120)] is obtained from Eq.(4.79)¹². The procedure of taking only the diagonal elements of L into account would not have been possible from Eq.(3.136). The reason is the non-local term, due to the screened interaction W . Therefore, one has to solve the full four-point BSE for L first, and take the diagonal elements only a posteriori.

The Coulomb divergence

We will now show, why the inclusion of the amputated Coulomb kernel into the Dyson equation for the two-point density-correlation function is necessary, when one aims to calculate the macroscopic dielectric function ϵ_M . From the definition of the microscopic dielectric function [see Eq.(H.3)], which reads in short form notation $\epsilon = 1 - vP$, the Dyson equation for χ can be rewritten (in reciprocal space) in the following way[62]:

$$\chi = P + Pv\chi \longleftrightarrow \chi = P + P\epsilon^{-1}vP. \quad (4.80)$$

In order to obtain now the macroscopic dielectric function, ϵ needs to be inverted first. Written in a matrix form in the reciprocal space, the microscopic dielectric function becomes

$$\epsilon = \begin{pmatrix} \epsilon_h & \epsilon_w^T \\ \epsilon_w & \epsilon_b \end{pmatrix}. \quad (4.81)$$

In Eq.(4.81) the head ϵ_h is given by the components $\mathbf{G} = \mathbf{G}' = 0$, while the wings ϵ_w and ϵ_w^T , and the body ϵ_b contains components with non-vanishing reciprocal lattice vectors $\mathbf{G}$:

$$\epsilon_h = 1 - v_0(\mathbf{q})P_{00}(\mathbf{q}) \quad (4.82)$$

$$\epsilon_w = -v_{\mathbf{G}}(\mathbf{q})P_{\mathbf{G}0}(\mathbf{q}) \quad (4.83)$$

$$\epsilon_w^T = -v_0(\mathbf{q})P_{0\mathbf{G}'}(\mathbf{q}) \quad (4.84)$$

$$\epsilon_b = \delta_{\mathbf{G}\mathbf{G}'} - v_{\mathbf{G}}(\mathbf{q})P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}). \quad (4.85)$$

¹²From the limes $4 \rightarrow 2$ and $3 \rightarrow 1$ the irreducible two-point polarizability P is obtained, thus $\tilde{L}(12; 12) \equiv P(12)$.

The inversion of the matrix in Eq.(4.81) can be calculated as shown in Refs.[62, 97]. One obtains for ϵ^{-1} the following matrix representation

$$\epsilon^{-1} = \begin{pmatrix} 0 & 0 \\ 0 & \epsilon_b^{-1} \end{pmatrix} + [\epsilon_h - \epsilon_w^T \epsilon_b^{-1} \epsilon_w]^{-1} \begin{pmatrix} 1 & -\epsilon_w^T \epsilon_b^{-1} \\ -\epsilon_b^{-1} \epsilon_w & \epsilon_b^{-1} \epsilon_w \epsilon_w^T \epsilon_b^{-1} \end{pmatrix}. \quad (4.86)$$

The macroscopic dielectric function ϵ_M after Wiser[82] and Adler[81] is calculated from the inverse of the head of the inverse microscopic dielectric function. Since the head is now simply given by the term $[\epsilon_h - \epsilon_w^T \epsilon_b^{-1} \epsilon_w]^{-1}$ in Eq.(4.86), it yields

$$\begin{aligned} \epsilon_M = \frac{1}{\epsilon_{00}^{-1}} &= 1 - v_0(\mathbf{q}) P_{00}(\mathbf{q}) - \sum_{\tilde{\mathbf{G}}, \tilde{\mathbf{G}}' \neq 0} v_0(\mathbf{q}) P_{0\tilde{\mathbf{G}}}(\mathbf{q}) \epsilon_b^{-1} \epsilon_{\tilde{\mathbf{G}}, \tilde{\mathbf{G}}'} v_{\tilde{\mathbf{G}}'}(\mathbf{q}) P_{\tilde{\mathbf{G}}'0}(\mathbf{q}) \\ &= 1 - v_0(\mathbf{q}) \left[P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) + \sum_{\tilde{\mathbf{G}}, \tilde{\mathbf{G}}' \neq 0} P_{\mathbf{G}\tilde{\mathbf{G}}}(\mathbf{q}) \epsilon_b^{-1} \epsilon_{\tilde{\mathbf{G}}, \tilde{\mathbf{G}}'} v_{\tilde{\mathbf{G}}'}(\mathbf{q}) P_{\tilde{\mathbf{G}}'\mathbf{G}'}(\mathbf{q}) \right]_{\mathbf{G}=\mathbf{G}'=0}. \end{aligned} \quad (4.87)$$

By inspection of the expression in brackets one observes a striking similarity with the expression of the two-point correlation function given on the rhs in Eq.(4.80) with the exception of missing the long-range components $\tilde{\mathbf{G}} = \tilde{\mathbf{G}}' = 0$. This problem, however, can be cured if the Coulomb kernel within the definition of the microscopic dielectric function is substituted by an amputated kernel

$$\bar{v}_{\mathbf{G}}(\mathbf{q}) = \begin{cases} 0 & \text{if } \mathbf{G} = 0 \\ v_{\mathbf{G}}(\mathbf{q}) & \text{if } \mathbf{G} \neq 0 \end{cases}. \quad (4.88)$$

This modification simplifies the inversion of the corresponding matrix $\bar{\epsilon}^{13}$ as it can be deduced from Eq.(4.86). One thus obtains

$$\bar{\epsilon}^{-1} = \begin{pmatrix} 1 & 0 \\ -\epsilon_b^{-1} \epsilon_w & \epsilon_b^{-1} \end{pmatrix} \quad (4.89)$$

By exploiting the modified inverse dielectric function [Eq.(4.89)], Eq.(4.87) can be rewritten in the following way

$$\epsilon_M = 1 - v_0(\mathbf{q}) \left[P_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) + \sum_{\tilde{\mathbf{G}}, \tilde{\mathbf{G}}'} P_{\mathbf{G}\tilde{\mathbf{G}}}(\mathbf{q}) \bar{\epsilon}_{\tilde{\mathbf{G}}, \tilde{\mathbf{G}}'}^{-1} v_{\tilde{\mathbf{G}}'}(\mathbf{q}) P_{\tilde{\mathbf{G}}'\mathbf{G}'}(\mathbf{q}) \right]_{\mathbf{G}=\mathbf{G}'=0} \quad (4.90)$$

or equivalently

$$\epsilon_M = 1 - v_0(\mathbf{q}) \bar{\chi}(\mathbf{q})_{00}. \quad (4.91)$$

In the latter equation we made use of the alternative formulation of the Dyson equation [Eq.(4.80)] with the amputated Coulomb kernel, i.e. $\bar{\chi} = P + P \bar{\epsilon}^{-1} \bar{v} P$. An alternative derivation for the macroscopic dielectric function is also given in section 8.1.

¹³The modified microscopic dielectric function is now given by $\bar{\epsilon} = 1 - \bar{v} P$.

4.1.11. Longitudinal or transverse dielectric function

Within the preceding sections, the dielectric function has been noticed to link the total potential to an arbitrary external potential. However, when talking about optical properties we are faced with electromagnetic fields as an external perturbation. The main difference between both perturbations is that an external charge distribution is related to a longitudinal field since the electric field $\mathbf{E}_{\text{ext}}$ is determined by the gradient of the corresponding external potential V_{ext} , i.e. $\mathbf{E}_{\text{ext}}(\mathbf{r}) = -\nabla_{\mathbf{r}} V_{\text{ext}}(\mathbf{r})$. On the other hand, the electric field of an electromagnetic wave is perpendicular to the direction of propagation and hence addresses a transverse external perturbation. However, both kinds of perturbations will in general induce longitudinal and transverse charge densities as well as current densities in the medium, respectively. This is accounted by the complex dielectric tensor $\hat{\epsilon}$ that relates the total electric field $\mathbf{E}$ to the external field, which is equivalent to the displacement field $\mathbf{D}$ in Maxwell's equations:

$$\mathbf{D} = \hat{\epsilon} \mathbf{E} \quad (4.92)$$

With respect to the cartesian coordinate system the dielectric function is a tensor with dimension 3×3 and rank 2. It consists of the components $\epsilon_{\alpha,\beta}$ with $\alpha, \beta = x, y, z$ denoting the cartesian x, y, z -directions. The total electric field $\mathbf{E}$ can, as it is known from classical electrodynamics, be decomposed into a longitudinal part $\mathbf{E}^{\text{L}}$ and a transverse part $\mathbf{E}^{\text{T}}$, respectively. Hence, Eq.(4.92) may be also written as

$$\begin{pmatrix} \mathbf{D}^{\text{L}} \\ \mathbf{D}^{\text{T}} \end{pmatrix} = \begin{pmatrix} \hat{\epsilon}^{\text{LL}} & \hat{\epsilon}^{\text{LT}} \\ \hat{\epsilon}^{\text{TL}} & \hat{\epsilon}^{\text{TT}} \end{pmatrix} \begin{pmatrix} \mathbf{E}^{\text{L}} \\ \mathbf{E}^{\text{T}} \end{pmatrix}. \quad (4.93)$$

Hereby, the individual components describe the purely longitudinal $\hat{\epsilon}^{\text{LL}}$, the purely transverse $\hat{\epsilon}^{\text{TT}}$ dielectric function, while the off-diagonal elements couple the transverse (longitudinal) induced electric field due to a longitudinal (transverse) external field. In order to relate the longitudinal and transverse components to the cartesian axes, one notes, that the dielectric tensor in Eq.(4.92) may be written as [98]

$$\hat{\epsilon} = \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{pmatrix}. \quad (4.94)$$

In order to project out the longitudinal part $\hat{\epsilon}^{\text{LL}}$ the tensor on the rhs of Eq.(4.94) will be multiplied with the dyadic $\mathbf{1}^{\text{L}}$ on both sides and similar for the remaining components in Eq.(4.93) one finds:

$$\hat{\epsilon}^{\text{LL}} = \mathbf{1}^{\text{L}} \cdot \hat{\epsilon} \cdot \mathbf{1}^{\text{L}} \quad (4.95)$$

$$\hat{\epsilon}^{\text{TT}} = \mathbf{1}^{\text{T}} \cdot \hat{\epsilon} \cdot \mathbf{1}^{\text{T}} \quad (4.96)$$

$$\hat{\epsilon}^{\text{LT}} = \mathbf{1}^{\text{L}} \cdot \hat{\epsilon} \cdot \mathbf{1}^{\text{T}} \quad \text{and} \quad \text{L} \leftrightarrow \text{T}. \quad (4.97)$$

From the definition of the longitudinal unit dyadic, i.e. $\mathbf{1}^{\text{L}} = \mathbf{q} \otimes \mathbf{q}/q^2$, one obtains the corresponding transverse unit dyadic by the relation $\mathbf{1}^{\text{T}} = \mathbf{1} - \mathbf{1}^{\text{L}}$, while $\mathbf{1}$ denotes the unit dyadic. In

practical applications the calculation of the dielectric function for optical properties goes along with the calculation of the longitudinal dielectric function $\hat{\epsilon}^{LL}$. Hereby, the static case is assumed, so that an external field induces only a static total electric total field. Therefore, the transverse part $\mathbf{E}^T$ is neglected.¹⁴ Equation (4.93) thus simplifies to

$$\mathbf{D}^L = \hat{\epsilon}^{LL} \mathbf{E}^L. \quad (4.98)$$

The question now arises, how can we link the longitudinal dielectric function to the transverse one, obtained by experimental measurements, e.g. by the reflectivity measurements. For isotropic media, like crystals with cubic symmetry, it has been proven that within the long wave length limit $\mathbf{q} \rightarrow 0$ the longitudinal and transverse components of $\hat{\epsilon}$ decouple. Even more, the components of the tensors $\hat{\epsilon}^{LL}(\mathbf{q} = 0)$ and $\hat{\epsilon}^{TT}(\mathbf{q} = 0)$ become equal, i.e. $\epsilon_{\alpha\beta}^{LL}(\mathbf{q} = 0) = \epsilon_{\alpha\beta}^{TT}(\mathbf{q} = 0)$ [81, 99]. In terms of the cartesian axes, one finds for an electromagnetic wave travelling in say x -direction the following relation:

$$\epsilon_{xx}^{LL}(q_x = 0) = \begin{cases} \epsilon_{yy}^{TT}(q_x = 0) \\ \epsilon_{zz}^{TT}(q_x = 0) \end{cases}. \quad (4.99)$$

For an arbitrary direction of the propagation vector $\mathbf{q}$, the longitudinal dielectric function is obtained by

$$\epsilon^{LL} = \hat{\mathbf{q}} \cdot \hat{\epsilon} \cdot \hat{\mathbf{q}}, \quad (4.100)$$

which, in the simplest case with $\hat{\mathbf{q}} = q \cdot \hat{\mathbf{e}}_x$, reduces to $\epsilon^{LL} = \epsilon_{xx}^{LL}$. Thus, electromagnetic waves in the optical long wave length limit, either longitudinal or transverse, become indistinguishable for an isotropic medium. For noncubic materials, the relation in Eq.(4.99), however, does not hold due to different symmetries along different crystal axes. Nevertheless, a comparison between the longitudinal and transverse dielectric function is still possible, as long as the direction of polarization of the medium, due to the electric field $\mathbf{D}$, is in the same direction for both modes of the external perturbation [98].

¹⁴If the underlying Maxwell equations are solved, even within the quasi-stationary case, the electric field $\mathbf{E}$ consists of a longitudinal (curl free) and a transverse (divergence free) part. The latter one is given by the time-derivative of the vector potential $\mathbf{A}$.

¹⁵For cubic materials, the dielectric tensor in Eq.(4.94) reduces to the diagonal components $\epsilon_{\alpha\beta} \delta_{\alpha,\beta}$, since the cartesian x, y, z -directions correspond to the principle axes.

5. Time-dependent density functional theory

In the previous section, we have demonstrated in what way the density response function can be calculated exploiting the Green's function formalism. Thereby, we have to calculate the so-called density fluctuation propagator that basically evolves the density fluctuation due to a weak external perturbation in time. However, the computation of the density response function involves not only the laborious calculation of accurate quasiparticle corrections due to the one particle Green's function but also the subsequent calculation of the four point quantity L . This has encouraged the development of a linear response theory footing on the density functional theory, namely the time-dependent density functional theory. It is the extension of the static ground state DFT to a formalism that covers the relation of a time-dependent density to a time-dependent external potential¹. This method allows formally to trace the density evolution in time starting from a previous calculated initial state of the many-body system. From the density variation with respect to the ground state density, one then obtains a route to calculate the density response function. In the following, the main features of time-dependent density functional theory shall be demonstrated as well as its applicability to solid state problems.

5.1. The Runge-Gross theorem

In order to construct a time-dependent formalism that incorporates the one-to-one mapping between the external potential and the density, one notes that a time-dependent external potential determines the corresponding time-dependent density due to the underlying Hamiltonian $\hat{H}(\{\mathbf{r}\}, t)$. The latter one consists of a kinetic part

$$\hat{T} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2, \quad (5.1)$$

the mutual Coulomb interaction

$$\hat{V}_{\text{int}} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (5.2)$$

and a time-dependent external potential

$$\hat{V}_{\text{ext}} = \sum_i V_{\text{ext}}(\mathbf{r}_i, t). \quad (5.3)$$

¹This one-to-one correspondence between time-dependent density and time-dependent external potential has been proved by the Runge and Gross. [100]

The dynamics of the many-body system is then completely determined by the time-dependent Schrödinger equation, i.e.

$$i\hbar \frac{\partial}{\partial t} \Psi(\{\mathbf{r}\}, t) = \hat{H}(\{\mathbf{r}\}, t) \Psi(\{\mathbf{r}\}, t), \quad \text{with } \Psi(\{\mathbf{r}\}, t_0) \text{ given} \quad (5.4)$$

where Ψ is the (interacting) many-body wave function that eventually yields the corresponding (interacting) electronic one-body density

$$\rho(\mathbf{r}, t) = N \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t)|^2. \quad (5.5)$$

Given the potential V_{ext} , it is always possible to solve the corresponding Schrödinger equation and thus establish the mapping from the external potential $V_{\text{ext}}(\mathbf{r}, t)$ to the density $\rho(\mathbf{r}, t)$. With the Runge-Gross theorem [100] the inverse mapping, i.e. $\rho(t) \mapsto V_{\text{ext}}(\mathbf{r}, t)$ has been proven, and concludes a unique one-to-one correspondence between the external potential and the density. The proof is based on the SEQ (5.4) and considers the time evolution of two different densities $\rho_1(t)$ and $\rho_2(t)$ under the influence of two different external potentials $V_{\text{ext},1}(\mathbf{r}, t)$ and $V_{\text{ext},2}(\mathbf{r}, t)$ that are supposed to differ by more than a purely time-dependent function $h(t)$:

$$V_{\text{ext},2}(\mathbf{r}, t) \neq V_{\text{ext},1}(\mathbf{r}, t) + h(t). \quad (5.6)$$

Furthermore, both densities are required to evolve from a fixed initial many-particle state $\Psi(t_0)$ at a finite time t_0 .⁴ Similar to the static DFT the question arises what are dismissible potentials for the time-dependent DFT. They are *a priori* supposed to be smoothly varying functions in time and are finite in the whole real space. Thus they are Taylor expandable about the initial time t_0 :

$$V_{\text{ext}}(\mathbf{r}, t) = \sum_{m=0}^{\infty} \frac{c_m(\mathbf{r})}{m!} (t - t_0)^m \quad \text{with} \quad c_m(\mathbf{r}) = \left. \frac{\partial}{\partial t^m} V_{\text{ext}}(\mathbf{r}, t) \right|_{t=t_0}. \quad (5.7)$$

Since the initial state $\Psi(t_0)$ is not required to be an eigenstate of the initial external potential $V_{\text{ext}}(t_0)$, external potentials that are switched on suddenly are also covered [101] and thus takes scenarios in spectroscopy into account, where an external perturbation is switched on at a given time $t = t_0$. Additionally, two potentials owing to the expansion in Eq.(5.7) will differ by more than a time dependent function $h(t)$ if some of the Taylor coefficients $c_{m,1}(\mathbf{r})$ and $c_{m,2}(\mathbf{r})$ differ by more than a constant. This translates to the fact that there exist an integer $m \geq 0$ such that the difference of the expansion coefficient $c_{m,1}(\mathbf{r}) - c_{m,2}(\mathbf{r}) \equiv w_m(\mathbf{r})$ from Eq.(5.7) is more than a trivial constant, but a spatial dependent function [102]:

$$c_{m,1}(\mathbf{r}) - c_{m,2}(\mathbf{r}) = \frac{\partial^m}{\partial t^m} [V_{\text{ext},1}(\mathbf{r}, t) - V_{\text{ext},2}(\mathbf{r}, t)]_{t=t_0} \neq \text{const}. \quad (5.8)$$

²The density shall be normalized to the total number of electrons N , i.e. $\int d\mathbf{r} \rho(\mathbf{r}, t) = N$.

³The addition of a purely time dependent function to the potential manifests in an additional phase factor in the many-particle wave function Ψ . Taking any expectation value such as the density $\rho = \langle \Psi | \hat{\rho} | \Psi \rangle$ will cancel the phase factor and yields the same density.

⁴For practical application this initial many-particle state is taken as the ground state. This, however, is not compulsory for the Runge-Gross theorem.

The following proof of the Runge-Gross theorem follows closely the references [101, 102, 103]. It makes use of the fact that during the time propagation the electronic charges are conserved. This is expressed by the continuity equation that links the time derivative of the electronic charge density ρ to the current density $\mathbf{j}$ as the following

$$\frac{\partial}{\partial t}\rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t). \quad (5.9)$$

In the first step, one may show that two different external potentials lead to two different current densities $\mathbf{j}_1(\mathbf{r}, t)$ and $\mathbf{j}_2(\mathbf{r}, t)$ immediately after the time evolution, i.e. for times $t > t_0$. From the rules of quantum mechanics, we exploit the time evolution of a quantum mechanical expectation value, i.e. $i\hbar \frac{d}{dt} \langle \hat{O}(t) \rangle = \langle [\hat{O}(t), \hat{H}(t)] \rangle + \langle \frac{\partial \hat{O}(t)}{\partial t} \rangle$ and apply this to the difference of the aforementioned current densities:

$$\begin{aligned} i\hbar \frac{d}{dt} \{\mathbf{j}_1(\mathbf{r}, t) - \mathbf{j}_2(\mathbf{r}, t)\} \Big|_{t=t_0} &= \langle \Psi_0 | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}_1(t_0) - \hat{H}_2(t_0)] | \Psi_0 \rangle \\ &= \langle \Psi_0 | [\hat{\mathbf{j}}(\mathbf{r}), \hat{V}_{\text{ext},1}(t_0) - \hat{V}_{\text{ext},2}(t_0)] | \Psi_0 \rangle \\ &= -i\rho(\mathbf{r}, t_0) \nabla [V_{\text{ext},1}(\mathbf{r}, t_0) - V_{\text{ext},2}(\mathbf{r}, t_0)] \\ &= -i\rho(\mathbf{r}, t_0) \nabla w_0(\mathbf{r}). \end{aligned} \quad (5.10)$$

Thereby, we have used the definition of the paramagnetic current density operator $\hat{\mathbf{j}}_p(\mathbf{r}, t)$ [101] that yields the time-dependent current density $\mathbf{j}(\mathbf{r}, t)$

$$\begin{aligned} \mathbf{j}(\mathbf{r}, t) &= \langle \Psi(t) | \hat{\mathbf{j}}_p(\mathbf{r}) | \Psi(t) \rangle \\ &= \frac{1}{2i} \langle \Psi(t) | \sum_{j=1}^N \nabla_j \delta(\mathbf{r} - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \nabla_j | \Psi(t) \rangle \\ &= \frac{N}{2i} \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \left\{ -\nabla \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \right. \\ &\quad \left. + \Psi^*(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \nabla \Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N, t) \right\}. \end{aligned} \quad (5.11)$$

If now the rhs of Eq.(5.10), i.e. the third line, differs already in the very first Taylor coefficient with $m = 0$, then $V_{\text{ext},1}(\mathbf{r}, t_0) - V_{\text{ext},2}(\mathbf{r}, t_0)$ cannot cancel due to the construction of both external potentials by Eq.(5.6). Hence, for an infinitesimally later time t with $t > t_0$, the two induced current densities $\mathbf{j}_1(\mathbf{r}, t)$ and $\mathbf{j}_2(\mathbf{r}, t)$ due to the two external potentials $V_{\text{ext},1}(\mathbf{r}, t_0)$ and $V_{\text{ext},2}(\mathbf{r}, t_0)$ are different. The same argument holds, if the smallest integer m in Eq.(5.8) is greater than zero. In this case a repeated application of the time derivative of Eq.(5.10) yields eventually

$$i\hbar \frac{d^{m+1}}{dt^{m+1}} \{\mathbf{j}_1(\mathbf{r}, t) - \mathbf{j}_2(\mathbf{r}, t)\} \Big|_{t=t_0} = -i\rho(\mathbf{r}, t) \nabla w_m(\mathbf{r}) \Big|_{t=t_0}. \quad (5.12)$$

If the function $w_m(\mathbf{r})$ does not vanish identically, then the two external potentials differ at least by one Taylor coefficient and thus the condition of deviating current densities for $t > t_0$ is fulfilled.

In a second step, it remains to show the difference of the corresponding current densities. For

this purpose one exploits the continuity equation (5.9) by taking the time derivative on both sides and obtains the following relation

$$\begin{aligned} \frac{\partial^{m+2}}{\partial t^{m+2}} [\rho_1(\mathbf{r}, t) - \rho_2(\mathbf{r}, t)]_{t=t_0} &= -\nabla \cdot \frac{\partial^{m+1}}{\partial t^{m+1}} [\mathbf{j}_1(\mathbf{r}, t) - \mathbf{j}_2(\mathbf{r}, t)]_{t=t_0} \\ &= \nabla \cdot [\rho(\mathbf{r}, t_0) \nabla w_m(\mathbf{r})]. \end{aligned} \quad (5.13)$$

The proof were complete without the divergence on the rhs in Eq.(5.13). For the sake of evidence, we follow again Ref.[102] and need to show that divergence does not render the rhs to zero in the equation above. By means of the Green's theorem the expression of interest is provided due to the relation

$$\int d\mathbf{r} \rho(\mathbf{r}, t_0) [\nabla w_m(\mathbf{r})]^2 = \int d\mathbf{r} w_m(\mathbf{r}) \nabla \cdot [\rho(\mathbf{r}, t_0) \nabla w_m(\mathbf{r})] + \oint df \cdot [\rho(\mathbf{r}, t_0) w_m(\mathbf{r}) \nabla w_m(\mathbf{r})]. \quad (5.14)$$

In the original proof [100, 102], the external potentials are assumed to be realizable by experiments and thus are generated by real and normalizable external charge densities. Thus, they fall off with $1/r$ and the surface integral on the rhs in Eq.(5.14) vanishes when $\mathbf{r}$ goes to infinity⁵. As by construction, the function $w_m(\mathbf{r})$ is a spatially varying function and not a constant, the lhs of Eq.(5.14) is strictly positive. Therefore, the first term on the rhs must be strictly positive as well and demonstrate that the divergence does not causes the rhs of Eq.(5.13) to become zero. This concludes the proof of the Runge-Gross theorem. For practical applications, one often deals with extended systems such as periodic crystals instead of finite systems as assumed in Runge-Gross theorem. However, the divergence term on the rhs of Eq.(5.13) can only vanish if the function $w_m(\mathbf{r})$ has the following expression [104]

$$w_m(\mathbf{r}) = w_m(\mathbf{r}_0) - \int_{\mathbf{r}_0}^{\mathbf{r}} \frac{\rho(\mathbf{r}_0, t_0)}{\rho(\mathbf{r}', t_0)} \mathbf{E}_m \cdot d\mathbf{r}', \quad (5.15)$$

where $\mathbf{E}_m$ is a constant vector and $\mathbf{r}_0$ is some arbitrary fixed space point. Since the density ρ is always a positive quantity, $w_m(\mathbf{r})$ increases continuously as one approaches large distances, i.e. $|\mathbf{r}| \rightarrow \infty$. This implies, however, that at least one of the external potentials $V_{\text{ext},1}(\mathbf{r}, t_0)$ or $V_{\text{ext},2}(\mathbf{r}, t_0)$ are infinite and disagrees with the condition of being Taylor expandable in the time domain. In summary, the one-to-one correspondence between the external potential and the time-dependent density implies a functional dependence of the external potential w.r.t. the density and vice versa. Thus, the knowledge of the time-dependent density specifies the external potential and eventually the complete Hamiltonian and also the many-body wave function $\Psi(t)$. The latter one is thus a functional of the density but also a functional of the initial many-body wave function $\Psi_0(t)$ due to the construction of the Runge-Gross theorem. In turn, every quantum mechanical observable is ultimately determined and is furthermore a unique function of the density and $\Psi_0(t)$. Clearly, the initial state dependence is a limiting factor⁶ and apart

⁵The proof assumes only finite systems where also the potentials are assumed to decay to zero as $\mathbf{r} \rightarrow \infty$.

⁶As the external potential is a functional of the initial state Ψ_0 , which generates the density ρ , the inversion of the Hamiltonian with a given wave function Ψ_0 may lead to unphysical potentials. This is associated to the

from general cases [105, 106], this limitation is resolved if the initial many-particle wave function is chosen as a non-degenerate ground state wave function Ψ_{gs} [102], as by virtue of the static Hohenberg-Kohn theorem, Ψ_{gs} is itself a unique functional of the (unperturbed) ground state density at time point t_0 .

5.2. Time-dependent Kohn-Sham equations

Having established the unique functional dependence between the time-dependent potential and corresponding density, the Runge-Gross theorem gives no prescription on how to obtain the desired time-dependent density. Therefore it would be advantageous to have a Kohn-Sham scheme similar to the static DFT case that can be adopted to the time-dependent scenario. The validity of it has been given by the van Leeuwen theorem[107]. It serves as the fundamental theorem that proves the existence of an alternative many-particle system with a different interaction term and a different but unique external potential that reproduces the same density as obtained from the original many-particle system. It further requires the initial state $\Psi'(t_0)$ to yield the original density ρ . In that manner, one can choose the interaction term V'_{inter} to be zero, thus generating an auxiliary non-interacting many-particle state $\Phi(t_0)$ yielding the interacting density ρ , such as in the static Kohn-Sham scheme. By the Runge-Gross theorem, the resulting external potential is then a unique functional of ρ up to a time-dependent function. This correspondence is also known as the *non-interacting* V -representability problem, because the Runge-Gross theorem only ensures the uniqueness of the functional dependence of the potential, but not its existence. If, however, such a potential exists, the van Leeuwen theorem then formally justifies the time-dependent Kohn-Sham approach. Under this assumption the interacting density can be obtained from

$$\rho(\mathbf{r}, t) = \sum_{j=1}^N |\varphi_j(\mathbf{r}, t)|^2, \quad (5.16)$$

where the Kohn-Sham orbitals $\varphi_j(\mathbf{r}, t)$ obey the time-dependent Kohn-Sham equation[101]

$$i\hbar \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_s[\rho](\mathbf{r}, t) \right] \varphi_j(\mathbf{r}, t), \quad (5.17)$$

including the wanted external potential $V_s[\rho](\mathbf{r}, t)$. The latter one is denoted as the time-dependent Kohn-Sham potential. Its explicit expression can, however, not be obtained by minimizing the total energy like in the static DFT, since the energy is not a conserved quantity in the time-dependent case. Instead, the variation principle can be applied to the action functional $A[\Psi]$

$$A[\Psi] = \int_{t_0}^{t_1} dt \langle \Psi(t) | i\hbar \frac{\partial}{\partial t} - \hat{H}(t) | \Psi \rangle. \quad (5.18)$$

It takes a stationary point at the exact many-body wave-function $\Psi(t)$, so that the variation $\frac{\delta A[\tilde{\Psi}(t)]}{\delta \langle \tilde{\Psi}(t) |} \Big|_{|\tilde{\Psi}(t)\rangle = |\Psi(t)\rangle}$ vanishes. As a result, the time-dependent Schrödinger equation (5.4) is then obtained. By virtue of the Runge-Gross theorem, the interacting many-body wave function is

v -representability problem.

mapped onto the interacting density. Thus the action integral [Eq.(5.18)] may be rewritten as a corresponding density functional $A[\Psi] \rightarrow A[\rho]$

$$A[\rho] = \int_{t_0}^{t_1} dt \langle \Psi[\rho](t) | i\hbar \frac{\partial}{\partial t} - \hat{H}(t) | \Psi[\rho](t) \rangle. \quad (5.19)$$

The true interacting density then makes the functional $A[\rho]$ stationary and can be obtained by solving the corresponding Euler equation

$$\frac{\delta A[\rho]}{\delta \rho(\mathbf{r}, t)} = 0. \quad (5.20)$$

In the spirit of the energy functional from the static DFT, the functional $A[\rho]$ may be decomposed into a universal functional $B[\rho]$ and the contribution from the external potential in the following way

$$A[\rho] = B[\rho] - \int_{t_0}^{t_1} dt \int d\mathbf{r} \rho(\mathbf{r}, t) V_{\text{ext}}(\mathbf{r}, t). \quad (5.21)$$

Hereby, $B[\rho]$ is defined as

$$B[\rho] = \int_{t_0}^{t_1} dt \langle \Psi[\rho](t) | i\hbar \frac{\partial}{\partial t} - \hat{T} - \hat{V}_{\text{int}} | \Psi[\rho](t) \rangle. \quad (5.22)$$

Similarly to the action functional $A[\rho]$ of the interacting density, an equivalent functional $A_s[\rho]$ for the non-interacting density can be formulated, including a universal functional $B_s[\rho]$ that reads

$$B_s[\rho] = \int_{t_0}^{t_1} dt \langle \Phi[\rho](t) | i\hbar \frac{\partial}{\partial t} - \hat{T} | \Phi[\rho](t) \rangle. \quad (5.23)$$

As this functional must become stationary at the true interacting density, its variation w.r.t the density needs to vanish as well. One thus obtains the condition

$$\frac{\delta A_s[\rho]}{\delta \rho(\mathbf{r}, t)} = \frac{\delta B_s[\rho]}{\delta \rho(\mathbf{r}, t)} - V_{\text{ext}}(\mathbf{r}, t) = 0. \quad (5.24)$$

By equation (5.24) the variation of the functional $B_s[\rho]$ at the true interacting density yields the wanted external potential of the non-interacting system, which can be identified as the time-dependent Kohn-Sham potential $V_s(\mathbf{r}, t)$. In order to obtain an explicit expression of the Kohn-Sham potential, the action integral may be decomposed into a suitable form by separating the time-dependent Hartree term from the mutual Coulomb interaction V_{int} . As a result, the action integral in Eq.(5.21) may be rewritten as

$$\begin{aligned} A[\rho](\mathbf{r}, t) = & B_s[\rho](\mathbf{r}, t) - \int_{t_0}^{t_1} dt \int d\mathbf{r} \rho(\mathbf{r}, t) V_{\text{ext}}(\mathbf{r}, t) \\ & - \frac{1}{2} \int dt \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r}, t) \rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} - A_{\text{xc}}[\rho], \end{aligned} \quad (5.25)$$

where the still unknown exchange-correlation part A_{xc} has been introduced. It contains, similar to the static DFT case, the difference of the non-interacting and interacting kinetic energy respectively, as well as all exchange and correlation effects and is a functional of the time-dependent density. The solution of the Euler equation (5.20) now allows formally to obtain the final expression of the Kohn-Sham potential

$$V_s(\mathbf{r}, t) = V_{\text{ext}}(\mathbf{r}, t) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r}, t)}, \quad (5.26)$$

including the time-dependent Hartree potential as the second term. The third term yields the time-dependent exchange-correlation potential $V_{xc}[\rho](\mathbf{r}, t)$ that causes, however, difficulties. First of all, one notices that the introduced action functional $A[\rho]$ [Eq.(5.18)] is not a unique functional of the time-dependent density, since the latter one determines the external potential only up to time-dependent constant. This constant is reflected by an additional phase factor in the many-particle wave function $\Psi[\rho]$. Although any expectation value $\langle \Psi[\rho] | \cdot | \Psi[\rho] \rangle$ remains unaffected due to the cancellation of the phase factor, the action integral is, however, affected. Therefore one needs to impose further boundary conditions on the many-particle wave function[108]. The more severe problem is encountered by the definition of the xc-potential. If one examines its variation w.r.t. the density, it can be performed only at previous times, i.e. the variation of the xc-potential can be affected only by densities at earlier times. This, however, results into a causality paradox[109, 101] as can be seen by the following relation:

$$\frac{\delta V_{xc}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}, t)} = \frac{\delta^2 A_{xc}[\rho]}{\delta \rho(\mathbf{r}, t) \delta \rho(\mathbf{r}', t')}. \quad (5.27)$$

While the left hand side of Eq.(5.27) is causal and thus nonzero only for $t > t'$, the right hand side is symmetric with respect to the time and space arguments $(\mathbf{r}, t)$ and $(\mathbf{r}', t')$. Thus causality contradicts the symmetry requirement and the xc-potential cannot (formally) be derived by the density variation of the functional A_{xc} , i.e. the last term in Eq.(5.26). This dilemma has been noted soon [101, 110] and several advanced methods have been derived to cure this problem. Among those solutions is the approach by van Leeuwen, who formulates a different action integral based on the Keldysh (pseudo-)time contour method[111]. Another formulation of a generalized action has been suggested by Mukamel[112] introducing so-called *Liouville space pathways*. These quantities have the desired time symmetry and may be derived from a generalized action integral. Furthermore, they yield the causal response function as given by Eq.(5.27). More recently, Vignale[113] gave reasons why theorems, although proved under the wrong assumption that V_{xc} is derivable as a functional derivative, turned out to be true. From a more elementary point of view, he showed that the original variation principle, i.e. $\delta A[\rho] = 0$, does not vanish but leads to an additional boundary term due to V -representability of the action integral $A[\rho]$.

5.3. Adiabatic approximation

In order to set up a complete density functional description of the interacting many-particle system, the discussion above shows that the time-dependent xc-potential needs to be approximated as it is still the unknown quantity in the Kohn-Sham approach. For real applications, one must note that the xc-potential has a functional dependence on the density of all times. This means it 'remembers' all densities from the past. This is a complicated task as one might need to store $\rho(t)$ at many time points and thus increases the computational effort. Therefore, the adiabatic approximation comes into play. It approximates the functional $V_{xc}[\rho](\mathbf{r}, t)$ in a way by ignoring the functional 'memory' of the past densities and one thus evaluates the xc-potential only at the instantaneous density:

$$V_{xc}^{\text{adiab}}[\rho](\mathbf{r}, t) = V_{xc}[\rho](\mathbf{r})|_{\rho=\rho(\mathbf{r}', t)}. \quad (5.28)$$

Moreover, to make the adiabatic approximation exact, the xc-potential is taken from static DFT, as this potential yields an exact expression if evaluated at the ground state density. If the external time-dependent potential obeys the adiabatic theorem of quantum mechanics, the many-particle system remains in its instantaneous eigenstate and the xc-potential can thus be evaluated at the density at the very same time t [114, 115, 103, 116], i.e.

$$V_{xc}^{\text{adiab}}[\rho](\mathbf{r}, t) = V_{xc}^{\text{sDFT}}[\rho_{\text{gs}}](\mathbf{r})|_{\rho_{\text{gs}}=\rho(\mathbf{r}', t)}. \quad (5.29)$$

With respect to the time argument, the xc-potential becomes a local function. This in turn has an immediate consequence for the xc-kernel f_{xc} . It is obtained as the density variation of the xc-potential as shown by Eq.(5.27) and reads in the adiabatic approximation

$$f_{xc}^{\text{adiab}}[\rho](\mathbf{r}, t; \mathbf{r}', t') = \frac{\delta V_{xc}^{\text{adiab}}[\rho](\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \delta(t - t'). \quad (5.30)$$

Thus, in the frequency domain, the resulting xc-kernel $f_{xc}^{\text{adiab}}(\omega)$ is then frequency-independent. That quantity is of particular interest in terms of the linear response theory applied to TDDFT and will be discussed in section 5.4.3. Although, the adiabatic approximation considers external potentials that are formally excluded (as they vary adiabatically slow in time) by the Runge-Gross theorem, it has become the working horse in current TDDFT applications as it is easy to compute and has given reliable results if weakly time-dependent phenomena are considered.

5.4. Linear response applied to TDDFT - excitation energies

In the previous section we already have introduced the concept of the linear response theory and have demonstrated how it applies to the many-body description within the Green's function formalism. In this section, the principles of the linear response theory shall be examined in terms of the time-dependent density functional theory. Besides the success of the Green's function formalism to calculate the density response function, TDDFT offers a much easier tool to calculate the same quantity, if only the exchange-correlation kernel were known exactly. In this work we

will also apply the TDDFT to calculate the density response function χ in the context of the time evolution method, shown in the following chapter 8.

The Dyson equation for χ

In the realm of the linear response theory, the external potential $V_{\text{ext}}(\mathbf{r}, t)$ can be decomposed, such that it contains a time-dependent part $\delta V_{\text{ext}}(\mathbf{r}, t)$ that is switched on at a particular time t_0 and the initial static external potential $V_{\text{ext}}(\mathbf{r})$ of the unperturbed system:

$$V_{\text{ext}}(\mathbf{r}, t) = \begin{cases} V_{\text{ext}}(\mathbf{r}) & \text{if } t < t_0 \\ V_{\text{ext}}(\mathbf{r}) + \delta V_{\text{ext}}(\mathbf{r}, t) & \text{if } t \geq t_0. \end{cases} \quad (5.31)$$

Due to the one-to-one correspondence between the interacting density ρ and the external potential by the Runge-Gross theorem [100], the functional dependence $\rho[V_{\text{ext}}]$ allows a Taylor expansion of the density ρ under the constraint of a sufficiently small time-dependent part $\delta V_{\text{ext}}(\mathbf{r}, t)$, i.e. $\rho(\mathbf{r}, t) = \rho(\mathbf{r}) + \delta\rho(\mathbf{r}, t) + \dots$. Hence techniques of the functional derivative can be applied to calculate the time-dependent density variation due to the time-dependent external potential. This is just the density response function χ of the interacting many-body system, i.e.

$$\chi(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \left. \frac{\delta\rho[V_{\text{ext}}](\mathbf{r}_1, t_1)}{\delta V_{\text{ext}}(\mathbf{r}_2, t_2)} \right|_{V_{\text{ext}}=V_{\text{ext}}(\mathbf{r})}. \quad (5.32)$$

The same arguments apply to the response of the non-interacting system. Here, the Kohn-Sham potential acts as the 'external' potential of the corresponding Kohn-Sham system [see also Eq.(5.24)]. Since the Runge-Gross theorem also holds in the case of non-interacting particles, i.e. we have the functional dependence $\rho[V_s]$, one obtains the response function of the non-interacting Kohn-Sham system as the following

$$\chi_{\text{KS}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \left. \frac{\delta\rho[V_s](\mathbf{r}_1, t_1)}{\delta V_s(\mathbf{r}_2, t_2)} \right|_{V_s=V_s[\rho_{\text{gs}}](\mathbf{r})}. \quad (5.33)$$

Since the density and thus the density variation $\delta\rho$ are the same in the real physical system as well in the Kohn-Sham system the corresponding response functions are ultimately connected. This might be shown using the chain rule of functional derivatives and applying this to Eq.(5.32):

$$\chi(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \int d\mathbf{r}_3 dt_3 \left. \frac{\delta\rho(\mathbf{r}_1, t_1)}{\delta V_s(\mathbf{r}_3, t_3)} \frac{\delta V_s(\mathbf{r}_3, t_3)}{\delta V_{\text{ext}}(\mathbf{r}_2, t_2)} \right|_{\rho_{\text{gs}}}. \quad (5.34)$$

The last term in Eq.(5.34) can be calculated explicitly, if the definition of the Kohn-Sham potential V_s [Eq.(5.26)] is exploited. One obtains

$$\begin{aligned} \left. \frac{\delta V_s(\mathbf{r}_1, t_1)}{\delta V_{\text{ext}}(\mathbf{r}_2, t_2)} \right|_{\rho_{\text{gs}}} &= \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(t_1 - t_2) \\ &+ \int d\mathbf{r}_3 dt_3 \left[\frac{\delta(t_1 - t_3)}{|\mathbf{r}_1 - \mathbf{r}_3|} + \left. \frac{\delta^2 A_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r}_1, t_1) \delta\rho(\mathbf{r}_3, t_3)} \right|_{\rho=\rho_{\text{gs}}} \right] \frac{\delta\rho(\mathbf{r}_3, t_3)}{\delta V_{\text{ext}}(\mathbf{r}_2, t_2)}, \end{aligned} \quad (5.35)$$

where the chain rule has been applied once more in the equation above. With the aid of Eq.(5.32) and Eq.(5.33) the density response function χ is finally obtained by substituting the expression of Eq.(5.35) into Eq.(5.34). As a result one ends up with a Dyson equation that reads

$$\begin{aligned} \chi(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = & \chi_{\text{KS}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) + \iint d\mathbf{r}_3 dt_3 d\mathbf{r}_4 dt_4 \chi_{\text{KS}}(\mathbf{r}_1 t_1, \mathbf{r}_3 t_3) \\ & \times \left[\frac{\delta(t_3 - t_4)}{|\mathbf{r}_3 - \mathbf{r}_4|} + \frac{\delta^2 A_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r}_3, t_3)\delta\rho(\mathbf{r}_4, t_4)} \Big|_{\rho=\rho_{\text{gs}}} \right] \chi(\mathbf{r}_4 t_4, \mathbf{r}_2 t_2). \end{aligned} \quad (5.36)$$

The expression in the square bracket contains two terms, the Hartree kernel (first term) and the exchange-correlation kernel f_{xc} as the second term, i.e.

$$f_{\text{xc}}[\rho](\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = \frac{\delta^2 A_{\text{xc}}[\rho]}{\delta\rho(\mathbf{r}_1, t_1)\delta\rho(\mathbf{r}_2, t_2)} \Big|_{\rho=\rho_{\text{gs}}} = \frac{\delta V_{\text{xc}}[\rho](\mathbf{r}_1, t_1)}{\delta\rho(\mathbf{r}_2, t_2)} \Big|_{\rho=\rho_{\text{gs}}}. \quad (5.37)$$

While the Kohn-Sham response function χ_{KS} can be expressed explicitly as shown below, the kernel f_{xc} requires an approximate expression. The most widely used approximation is the adiabatic approximation as already discussed in section 5.3. With respect to Eq.(5.30) the choice of a suitable approximation of the static exchange-correlation potential then depends on the many-particle system of interest.

Excitation energies

In order to calculate the excitation properties of a given many-particle system, we have shown in the previous chapter that the poles of the frequency dependent density response function $\chi(\omega)$ yield the desired excitation energies. Concerning the external and time-dependent potential within the TDDFT framework, only Taylor expandable potential with respect to the time argument are admissible. Among those potentials, there are such ones that are switched on suddenly. This is mathematically realized by the introduction of a theta function like in Eq.(4.1). However, this kind of perturbation causes a subtle problem. As one aims to calculate the excitation energies of the physical system of interest, one actually wants to measure the resonances of the system. Following the arguments in Refs. [41, 42], a suddenly switched on perturbation due to an external field will cause, however weak it is, a deformation of the wave function of the system. Such a perturbation will effectively heat up the system by transferring energy to it. Hence, the wave function is modified to an extent that does not allow to describe the time dependent wave function in linear order with respect to the perturbation, since non-linear effects might occur. Hence, the wave function suffers from a permanent deformation. In contrast to it, an adiabatically switched on perturbation yields only a reversible deformation of the wave function, while the boundary conditions of the wave function remains unchanged, i.e. the wave function turns back to its ground state as the lower bound t_0 of the time integral in Eq.(4.2) goes to minus infinity if the perturbation is modified with an extra factor $e^{\eta t}$. As we will see in the following, an adiabatically switched perturbation yields the real retarded response function $\chi^{\text{ret}}(\omega)$ [102], the same expression one would obtain by imposing a theta function to the external perturbation a

priori. In view of the Runge-Gross theorem, adiabatically switched on time-dependent potentials are excluded and the set of admissible potentials needs to be extended. A discussion on that topic about V -representability within linear response and the resulting issues on that can be found e.g. in Refs. [117] and [118]. We now focus on the exact expression of the density response function $\chi(\omega)$ that relates the density variation $\delta\rho$ to an external perturbation δV_{ext} . To within linear order of the external potential we have the following relation

$$\delta\rho(\mathbf{r}_1 t_1) = \iint d\mathbf{r}_2 dt_2 \chi(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) \delta V_{\text{ext}}(\mathbf{r}_2 t_2) \quad (5.38)$$

that results from the functional derivative given by Eq.(5.32). The density variation may be obtained from the difference

$$\delta\rho(\mathbf{r}, t) = \langle \Psi(t) | \hat{\rho} | \Psi(t) \rangle - \langle \Psi(t_0) | \hat{\rho} | \Psi(t_0) \rangle, \quad (5.39)$$

with the time-dependent wave function that obeys the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = [\hat{H} + \hat{H}'(t)] |\Psi(t)\rangle. \quad (5.40)$$

Here, $\hat{H}$ is the Hamiltonian of the unperturbed system, while $\hat{H}'(t)$ denotes the time-dependent perturbation. Within the adiabatic treatment, the perturbation shall additionally couple to the density of the many-particle system and thus takes the explicit form [42]

$$\hat{H}'(t) = \frac{1}{2\pi} \iint d\mathbf{r}' d\omega \delta V_{\text{ext}}(\mathbf{r}', \omega) e^{-i\omega t} e^{\eta t} \hat{\rho}(\mathbf{r}') + c.c.. \quad (5.41)$$

The complex conjugated term in Eq.(5.41) ensures the potential to be a real function. Under the condition of a small perturbation, which is usually enforced by an additional parameter λ , the time evolution of the wave function $|\Psi(t)\rangle$ is governed by the corresponding time evolution operator $\hat{U}(t, t_0)$ that is introduced in Eq.(D.16). Working within the Schrödinger picture and exploiting the principles of time-dependent perturbation theory [see e.g. Ref.[119]], the wave function $|\Psi(t)\rangle$ is expressed in terms of the unperturbed and time-dependent eigenstates $|\Psi_j^0(t)\rangle = |\Psi_j^0(t_0)\rangle e^{-\frac{i}{\hbar} E_j(t-t_0)}$ that corresponds to the unperturbed Hamiltonian $\hat{H}$. One eventually finds:

$$\begin{aligned} |\Psi_i(t)\rangle &= \sum_j |\Psi_j^0(t)\rangle \langle \Psi_j^0(t) | \hat{U}(t, t_0) | \Psi_i^0(t_0) \rangle \\ &= |\Psi_i^0(t)\rangle + \frac{\lambda}{i\hbar} \int_{-\infty}^t dt' |\Psi_j^0(t)\rangle \langle \Psi_j^0(t') | \hat{H}'(t') | \Psi_i^0(t') \rangle \\ &= |\Psi_i^0(t)\rangle + \lambda \sum_{j \neq i} c_j(t) |\Psi_j^0(t)\rangle, \end{aligned} \quad (5.42)$$

with the unperturbed initial wave function denoted by $|\Psi_i^0(t_0)\rangle$. Furthermore, the lower bound of the time integral has been taken as $-\infty$ to comply with the adiabatically switched on perturbation

$\hat{H}'(t)$. The transition coefficient $c_j(t)$ in Eq.(5.42) become with the aid of Eq.(5.41)

$$\begin{aligned} c_j(t) &= \frac{1}{i\hbar} \frac{1}{2\pi} \int_{-\infty}^t dt' \iint d\mathbf{r}' d\omega \delta V_{\text{ext}}(\mathbf{r}', \omega) e^{-i\omega t'} e^{i\eta t'} e^{i(\omega_j - \omega_i)(t' - t_0)} \langle \Psi_j^0(t_0) | \hat{\rho}(\mathbf{r}') | \Psi_i^0(t_0) \rangle \\ &= \frac{1}{\hbar} \frac{1}{2\pi} \iint d\mathbf{r}' d\omega \delta V_{\text{ext}}(\mathbf{r}', \omega) \frac{e^{-i[\omega + i\eta - (\omega_j - \omega_i)]t}}{\omega - (\omega_j - \omega_i) + i\eta} \langle \Psi_j^0(t_0) | \hat{\rho}(\mathbf{r}') | \Psi_i^0(t_0) \rangle e^{-i(\omega_j - \omega_i)t_0} \\ &\quad + [\omega \rightarrow -\omega]. \end{aligned} \quad (5.43)$$

The last exponential term in Eq.(5.43) can be safely set to 1. This phase factor stems from the phase oscillation of the unperturbed eigenstates of $\hat{H}$. Due to the adiabatic boundary conditions at $t_0 \rightarrow -\infty$, these eigenstates are simply the static eigenstates and thus have no phase oscillations. The resulting density variation $\delta\rho(\mathbf{r}, t)$ due to Eq.(5.39) computes to first order in the parameter λ as the following

$$\delta\rho(\mathbf{r}, t) = \lambda [\langle \Psi_i^0(t) | \hat{\rho}(\mathbf{r}) | \Psi_j^0(t) \rangle c_j(t) + c_j^*(t) \langle \Psi_j^0(t) | \hat{\rho}(\mathbf{r}) | \Psi_i^0(t) \rangle]. \quad (5.44)$$

Taking into account the explicit expression for the coefficients $c_j(t)$ as well as the phase factors of the matrix elements of Eq.(5.44) one finally obtains [42]

$$\begin{aligned} \delta\rho(\mathbf{r}, t) &= \frac{1}{2\pi\hbar} \iint d\mathbf{r}' d\omega \delta V_{\text{ext}}(\mathbf{r}', \omega) e^{-i(\omega + i\eta)t} \times \\ &\quad \times \sum_{j \neq i} \left[\frac{\langle \Psi_i^0 | \hat{\rho}(\mathbf{r}) | \Psi_j^0 \rangle \langle \Psi_j^0 | \hat{\rho}(\mathbf{r}') | \Psi_i^0 \rangle}{\omega - (\omega_j - \omega_i) + i\eta} - \frac{\langle \Psi_i^0 | \hat{\rho}(\mathbf{r}') | \Psi_j^0 \rangle \langle \Psi_j^0 | \hat{\rho}(\mathbf{r}) | \Psi_i^0 \rangle}{\omega + (\omega_j - \omega_i) + i\eta} \right] \end{aligned} \quad (5.45)$$

or equivalently in frequency space

$$\delta\rho(\mathbf{r}, \omega) = \int d\mathbf{r}' \delta V_{\text{ext}}(\mathbf{r}', \omega) \sum_{j \neq i} \left[\frac{\langle \Psi_i^0 | \hat{\rho}(\mathbf{r}) | \Psi_j^0 \rangle \langle \Psi_j^0 | \hat{\rho}(\mathbf{r}') | \Psi_i^0 \rangle}{\hbar\omega - (E_j - E_i) + i\hbar\eta} - \frac{\langle \Psi_i^0 | \hat{\rho}(\mathbf{r}') | \Psi_j^0 \rangle \langle \Psi_j^0 | \hat{\rho}(\mathbf{r}) | \Psi_i^0 \rangle}{\hbar\omega + (E_j - E_i) + i\hbar\eta} \right]. \quad (5.46)$$

From Eq.(5.46) one finally deduces the (retarded) density response function that is given by

$$\begin{aligned} \chi^{\text{ret}}(\mathbf{r}, \mathbf{r}' | \omega) &= \frac{\delta\rho(\mathbf{r}, \omega)}{\delta V(\mathbf{r}', \omega)} \\ &= \sum_{j \neq i} \left[\frac{\langle \Psi_i^0 | \hat{\rho}(\mathbf{r}) | \Psi_j^0 \rangle \langle \Psi_j^0 | \hat{\rho}(\mathbf{r}') | \Psi_i^0 \rangle}{\hbar\omega - (E_j - E_i) + i\hbar\eta} - \frac{\langle \Psi_i^0 | \hat{\rho}(\mathbf{r}') | \Psi_j^0 \rangle \langle \Psi_j^0 | \hat{\rho}(\mathbf{r}) | \Psi_i^0 \rangle}{\hbar\omega + (E_j - E_i) + i\hbar\eta} \right] \end{aligned} \quad (5.47)$$

Kohn-Sham response function

We will now shortly sketch how to calculate the Kohn-Sham response function $\chi_{\text{KS}}(\mathbf{r}, \omega)$. Since by assumption the density variation of the interacting system, as well as, that of the non-interacting system are identical, one may obtain the KS response function from Eq.(5.47). At a glance at Eq.(5.47), the many-particle states $|\Psi_i^0\rangle$ and $|\Psi_j^0\rangle$ can be described as a single Slater determinant, respectively, if we are concerned with non-interacting particles like in the Kohn-Sham system. In

general, an arbitrary determinantal state that refers to an antisymmetric fermionic wave function $|\Psi^a\rangle$ has the following expression:

$$|\Psi^a\rangle \equiv |\Psi^a(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N)\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{\nu_1}(\mathbf{r}_1, \sigma_1) & \varphi_{\nu_1}(\mathbf{r}_2, \sigma_2) & \dots & \varphi_{\nu_1}(\mathbf{r}_N, \sigma_N) \\ \varphi_{\nu_2}(\mathbf{r}_1, \sigma_1) & \varphi_{\nu_2}(\mathbf{r}_2, \sigma_2) & \dots & \varphi_{\nu_2}(\mathbf{r}_N, \sigma_N) \\ \vdots & \vdots & \dots & \vdots \\ \varphi_{\nu_N}(\mathbf{r}_1, \sigma_1) & \varphi_{\nu_N}(\mathbf{r}_2, \sigma_2) & \dots & \varphi_{\nu_N}(\mathbf{r}_N, \sigma_N) \end{vmatrix}, \quad (5.48)$$

where the one-particle orbitals $\varphi_{\nu_i}(\mathbf{r}, \sigma)$ can be identified as the corresponding Kohn-Sham orbitals with the spatial argument $\mathbf{r}$, the spin argument σ and the index ν_i that denotes a given set of quantum numbers as previously described due to Eq.(3.53). The corresponding spin part $f_{\nu_i}(\sigma)$ allows to give the most general spin state of the orbital $\varphi_{\nu_i}(\mathbf{r}, \sigma)$ as a linear combination of the two possible spin states, i.e. $f_{\nu_i} = c_{\uparrow} f_{\nu_i, \uparrow} + c_{\downarrow} f_{\nu_i, \downarrow} = \begin{pmatrix} c_{\uparrow} \\ c_{\downarrow} \end{pmatrix}$. Here we have used the spinor notation [see. e.g. Ref. [120]], and $c_{\uparrow}$ and $c_{\downarrow}$ denote the probability to find an electron with spin 'up' or 'down', respectively. Therefore, the orbital $\varphi_{\nu_i}(\mathbf{r}, \sigma)$ has two components and the index number N in Eq.(5.48) may be reduced to $M = N/2$. With the aid of the explicit determinantal expression, we note that the excited states $|\Psi_j^0\rangle$ differ from the ground state $|\Psi_i^0\rangle$ by one index ν_i , corresponding to the promotion of one electron into the unoccupied manifold. While in the ground state the N orbitals are distributed over the indices ν_i with $i \leq M$, it is one orbital that takes an index ν_j with $j > M$ in the excited state $|\Psi_j^0\rangle$. Furthermore, the spin-orbitals are orthogonal so that the matrix elements in Eq.(5.47) then read

$$\begin{aligned} \langle \Psi_j^0 | \hat{\rho}(\mathbf{r}) | \Psi_i^0 \rangle &= \langle \varphi_{\nu_1}(\mathbf{r}_1) \dots \varphi_{\nu_j}(\mathbf{r}_l) \dots \varphi_{\nu_M}(\mathbf{r}_M) | \sum_l \delta(\mathbf{r} - \mathbf{r}_l) | \varphi_{\nu_1}(\mathbf{r}_1) \dots \varphi_{\nu_i}(\mathbf{r}_l) \dots \varphi_{\nu_M}(\mathbf{r}_M) \rangle \\ &= \varphi_{\nu_j}^*(\mathbf{r}) \varphi_{\nu_i}(\mathbf{r}) \quad \text{with } j > M. \end{aligned} \quad (5.49)$$

In order to shorten the notation, we use in the following the index i for an occupied state and the index a for an unoccupied state, respectively. From Eq.(5.47), the Kohn-Sham response function results and reads

$$\chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\substack{i \in \text{occ} \\ a \in \text{unocc}}} \frac{\varphi_i^*(\mathbf{r}) \varphi_a(\mathbf{r}) \varphi_a^*(\mathbf{r}') \varphi_i(\mathbf{r}')}{\hbar\omega - (\varepsilon_a - \varepsilon_i) + i\hbar\eta} - \frac{\varphi_i^*(\mathbf{r}') \varphi_a(\mathbf{r}') \varphi_a^*(\mathbf{r}) \varphi_i(\mathbf{r})}{\hbar\omega + (\varepsilon_a - \varepsilon_i) + i\hbar\eta}. \quad (5.50)$$

In the equation above, the eigenvalue ε_i correspond to the static eigenfunction $\varphi_i(\mathbf{r})$ of the unperturbed Hamiltonian $\hat{H}$, i.e. the static Kohn-Sham Hamiltonian. Their difference results from the energy difference of the excited state with energy E_j and the ground state energy E_i in the denominator of Eq.(5.47) due to the underlying non-interacting Kohn-Sham particles. By inspection of Eqs.(5.50) and (5.47) the excitation energies of the non-interacting and interacting system are the poles of the corresponding density response function. Both expressions are very similar to their time-ordered counterparts and differ only by the complex term $+i\eta$ in the denominator. In the retarded expressions, the excitation energies are of course real quantities as well and one needs to take the limes $\eta \rightarrow 0^+$ in Eq.(5.50) and Eq.(5.47) that is missing in

both equations a priori. However, this limit can be performed and is related to the fact that the energy transfer due to the perturbation takes place until the time $t = \frac{1}{\eta}$. This time rate becomes infinitely long as η goes to zero. Hence, in the ideal adiabatic process, no energy is transferred to the system if $\eta \rightarrow 0^+$ [42]⁷.

5.4.1. Calculation of the excitation energies from χ^{ret}

In order to calculate explicitly the excitation energies, i.e. the poles of the density response function χ^{ret} , one makes use of the fact that the density response $\delta\rho(\mathbf{r}, \omega)$ has poles at the true excitation energies, now denoted as Ω . This can be readily seen from the definition of the density response function [Eq.(5.39)] that reads in frequency space

$$\delta\rho(\mathbf{r}_1, \omega) = \int d\mathbf{r}_2 \chi(\mathbf{r}_1, \mathbf{r}_2|\omega) \delta V_{\text{ext}}(\mathbf{r}_2, \omega). \quad (5.51)$$

On the other hand, the same density variation is linked to the density response function of the non-interacting Kohn-Sham system through the variation of the Kohn-Sham potential

$$\delta\rho(\mathbf{r}_1, \omega) = \int d\mathbf{r}_2 \chi_{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2|\omega) \delta V_{\text{s}}(\mathbf{r}_2, \omega). \quad (5.52)$$

The variation $\delta V_{\text{s}}(\mathbf{r}_2, \omega)$ is readily derived when looking at Eq.(5.26) and Fourier transforming to frequency space. One thus obtains

$$\delta V_{\text{s}}(\mathbf{r}_1, \omega) = V_{\text{ext}}(\mathbf{r}, \omega) + \int d\mathbf{r}_2 \left[\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{\text{xc}}(\mathbf{r}_1, \mathbf{r}_2|\omega) \right] \delta\rho(\mathbf{r}_2, \omega). \quad (5.53)$$

One notes that the combination of Eq.(5.52) and Eq.(5.53) yields a self-consistent equation for the density variation $\delta\rho$. After some straightforward algebraic manipulations one finds the following relation

$$\begin{aligned} & \int d\mathbf{r}_3 \left\{ \delta(\mathbf{r}_2 - \mathbf{r}_3) - \int d\mathbf{r}_2 \chi_{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2|\omega) \left[\frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} + f_{\text{xc}}(\mathbf{r}_2, \mathbf{r}_3|\omega) \right] \right\} \delta\rho(\mathbf{r}_3, \omega) \\ &= \int d\mathbf{r}_2 \chi_{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2|\omega) V_{\text{ext}}(\mathbf{r}_2, \omega). \end{aligned} \quad (5.54)$$

More importantly, the integral operator in curly brackets on the left hand side has to cancel out the poles of $\delta\rho(\mathbf{r}, \omega)$, i.e. when $\omega \rightarrow \Omega$, to make the right hand side of Eq.(5.54) finite. The latter one becomes infinite only at the Kohn-Sham excitation energies, but not at the exact energies Ω . Hence the necessary condition for this integral operator is to have zero eigenvalues if $\omega = \Omega$. In other words, one needs to solve the corresponding eigenvalue problem

$$\iint d\mathbf{r}_2 d\mathbf{r}_3 \chi_{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2|\omega) \left[\frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} + f_{\text{xc}}(\mathbf{r}_2, \mathbf{r}_3|\omega) \right] \zeta(\mathbf{r}_3, \omega) = \lambda(\omega) \zeta(\mathbf{r}_1, \omega) \quad (5.55)$$

⁷We may note that the external potential contributes to the energy transfer at first glance. That is why the introduced parameter λ is chosen to keep this energy contribution due to the external potential as small as possible [42]. In the ideal adiabatic case the perturbation is supposed to go to zero.

obeying the condition $\lambda(\Omega) = 1$. The solution of the eigenvalue problem can be performed either by choosing a real space basis such as it is given by Eq.(5.55) or one chooses a basis within a transition space with basis elements defined as the product of occupied and unoccupied orbitals. The latter choice becomes clear if the eigenvalue problem of Eq.(5.55) is modified as discussed e.g. in the Refs.[101, 121]. If one considers the definition of the orbital transition pair $\Phi_{ml}(\mathbf{r}) := \varphi_m^*(\mathbf{r})\varphi_l(\mathbf{r})$, the explicit expression of the Kohn-Shame response function [Eq.(5.50)] may be rewritten as the following:

$$\chi_{\text{KS}}(\mathbf{r}_1, \mathbf{r}_2|\omega) = (f_l - f_m) \sum_{m,l} \frac{\Phi_{ml}^*(\mathbf{r}_1)\Phi_{ml}(\mathbf{r}_2)}{\hbar\omega - (\varepsilon_m - \varepsilon_l) + i\hbar\eta}. \quad (5.56)$$

The indices m, l now denote occupied and unoccupied orbital states respectively, and f_n is the Fermi occupation number. Hence, the eigenvalue problem from Eq.(5.55) reduces to

$$\sum_{m,l} \frac{(f_l - f_m) \Phi_{ml}^*(\mathbf{r}_1)}{\hbar\omega - (\varepsilon_m - \varepsilon_l) + i\hbar\eta} \gamma_{ml}(\omega) = \lambda(\omega) \zeta(\mathbf{r}_1|\omega), \quad (5.57)$$

including the definition

$$\gamma_{ml}(\omega) = \iint d\mathbf{r}_2 d\mathbf{r}_3 \Phi_{ml}(\mathbf{r}_2) \left[\frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} + f_{\text{xc}}(\mathbf{r}_2, \mathbf{r}_3|\omega) \right] \zeta(\mathbf{r}_3|\omega). \quad (5.58)$$

The solution for the eigenvector $\zeta(\mathbf{r}_1, \omega)$ from Eq.(5.57) may be substituted into Eq.(5.58) to obtain a self-consistent expression for the coefficient $\gamma_{ml}(\omega)$

$$\begin{aligned} \gamma_{ml}(\omega) &= \iint d\mathbf{r}_2 d\mathbf{r}_3 \Phi_{ml}(\mathbf{r}_2) \left[\frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} + f_{\text{xc}}(\mathbf{r}_2, \mathbf{r}_3|\omega) \right] \times \\ &\times \sum_{m',l'} \frac{(f_{l'} - f_{m'}) \Phi_{m'l'}^*(\mathbf{r}_3)}{\hbar\omega - (\varepsilon_{m'} - \varepsilon_{l'}) + i\hbar\eta} \gamma_{m'l'}(\omega) \lambda^{-1}(\omega) \end{aligned} \quad (5.59)$$

from which the transformed eigenvalue problem of Eq.(5.55) into the transition space is gained:

$$\begin{aligned} \sum_{m',l'} \left[(\varepsilon_m - \varepsilon_l) \delta_{m,m'} \delta_{l,l'} + (f_{l'} - f_{m'}) \iint d\mathbf{r}_2 d\mathbf{r}_3 \Phi_{ml}(\mathbf{r}_2) f_{\text{Hxc}}(\mathbf{r}_2, \mathbf{r}_3|\Omega) \Phi_{m'l'}^*(\mathbf{r}_3) \right] \beta_{m'l'} \\ = \hbar\Omega \beta_{ml} \end{aligned} \quad (5.60)$$

This particular form as given by the equation above, though, can be further simplified since the index pair ml can be chosen either to describe the transition between the occupied and unoccupied manifold, i.e. by the transition pair ai and the opposite direction as given by the

index ia , only. Thus, Eq.(5.60) yields two coupled equations

$$\sum_{\substack{j \in \text{occ} \\ b \in \text{unocc}}} \left\{ [(\varepsilon_i - \varepsilon_a) \delta_{a,b} \delta_{i,j} - \mathcal{K}_{ia,jb}(\Omega)] \beta_{jb} + \mathcal{K}_{ia,bj}(\Omega) \beta_{bj} \right\} = \hbar \Omega \beta_{ia} \quad (5.61)$$

$$\sum_{\substack{j \in \text{occ} \\ b \in \text{unocc}}} \left\{ -\mathcal{K}_{ai,jb}(\Omega) \beta_{jb} + [(\varepsilon_a - \varepsilon_i) \delta_{a,b} \delta_{i,j} + \mathcal{K}_{ai,bj}(\Omega)] \beta_{bj} \right\} = \hbar \Omega \beta_{ai}. \quad (5.62)$$

To make this set of equations more symmetric, we let $X_{(ia)} = \beta_{ia}$ and $Y_{ai} = -\beta_{ai}$ and obtain

$$\sum_{\substack{j \in \text{occ} \\ b \in \text{unocc}}} \left\{ [-(\varepsilon_a - \varepsilon_i) \delta_{a,b} \delta_{i,j} - \mathcal{K}_{ia,jb}(\Omega)] X_{jb} - \mathcal{K}_{ia,bj}(\Omega) Y_{bj} \right\} = \hbar \Omega X_{ia} \quad (5.63)$$

$$\sum_{\substack{j \in \text{occ} \\ b \in \text{unocc}}} \left\{ -\mathcal{K}_{ai,jb} X_{jb} + [-(\varepsilon_a - \varepsilon_i) \delta_{a,b} \delta_{i,j} - \mathcal{K}_{ai,bj}(\Omega)] Y_{bj} \right\} = -\hbar \Omega Y_{ai}, \quad (5.64)$$

and further the compact notation [103]

$$\begin{pmatrix} \mathbf{A}(\Omega) & \mathbf{B}(\Omega) \\ \mathbf{B}^*(\Omega) & \mathbf{A}^*(\Omega) \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \hbar \Omega \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}. \quad (5.65)$$

where

$$\mathcal{K}_{ia,jb}(\Omega) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi_i^*(\mathbf{r}_1) \varphi_a(\mathbf{r}_1) f_{\text{Hxc}}(\mathbf{r}_1, \mathbf{r}_2 | \Omega) \varphi_j(\mathbf{r}_2) \varphi_b^*(\mathbf{r}_2) \quad (5.66)$$

$$\mathbf{A}_{ia,jb}(\Omega) = -\delta_{a,b} \delta_{i,j} (\varepsilon_a - \varepsilon_i) - \mathcal{K}_{ia,jb}(\Omega) \quad (5.67)$$

$$\mathbf{B}_{ia,jb}(\Omega) = -\mathcal{K}_{ia,bj}(\Omega) \quad (5.68)$$

By Eq.(5.65) we have found the central equation from which in principle excitation energies within the linear response regime are computable. One many note, however, that the given expression for the kernel $\mathcal{K}$ itself depends on the solution of the eigenvalue problem due to its Ω -dependence. Thus, some kind of iterative method needs to be applied. For practical applications, the exchange-correlation kernel f_{xc} is chosen within the adiabatic approximation and thus loses any frequency dependence and so does $\mathcal{K}$. Moreover, if the Kohn-Sham orbitals $\varphi_m(\mathbf{r})$ are additionally real valued, the resulting matrices $\mathbf{A}, \mathbf{B}$ become real as well turning the entire matrix on the left hand side of Eq.(5.65) to an Hermitian matrix.

5.4.2. Casida approach and the macroscopic polarizability

The very first derivation to calculate the excitation energies Ω was given by Casida[122, 123] in his seminal work. We want to demonstrate shortly his idea, as the solution of the resulting Casida equation is the state of the art method when it comes to solving excitation properties within the TDDFT. Casida's ansatz is based on the expression of the density variation in terms of the unperturbed Kohn-Sham orbitals that result in the so-called Kohn-Sham density matrix

$\delta\rho_{ml}(\omega)$. This density matrix is readily obtained from Eq.(5.52) as it gives the relation

$$\begin{aligned}\delta\rho(\mathbf{r}_1, \omega) &= \left[\sum_{m,l} \frac{(f_l - f_m)}{\hbar\omega - (\varepsilon_m - \varepsilon_l) + i\hbar\eta} \int d\mathbf{r}_2 \varphi_m^*(\mathbf{r}_2) \varphi_l(\mathbf{r}_2) \delta V_s(\mathbf{r}_2, \omega) \right] \varphi_m(\mathbf{r}_1) \varphi_l^*(\mathbf{r}_1) \\ &= \sum_{m,l} \delta\rho_{ml}(\omega) \varphi_m(\mathbf{r}_1) \varphi_l^*(\mathbf{r}_1).\end{aligned}\quad (5.69)$$

The expansion of the density as given by Eq.(5.69) may be used to express the variation of the Kohn-Sham potential δV_s [Eq.(5.35)] in terms of the Kohn-Sham density matrix. As a result one obtains the same working equation [see Eq.(J.4)] that is identical to Eq.(5.60) except for the additional term due to the external potential. As Casida assumes the Kohn-Sham orbitals as real quantities, the density response [Eq.(5.69)] recasts into the following matrix equation

$$\left[\begin{pmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}(\omega) & \mathbf{A}(\omega) \end{pmatrix} - \hbar\omega \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \right] \begin{pmatrix} \delta\rho(\omega) \\ \delta\rho^*(\omega) \end{pmatrix} = \begin{pmatrix} \mathbf{V}_{\text{ext}}(\omega) \\ \mathbf{V}_{\text{ext}}^*(\omega) \end{pmatrix}, \quad (5.70)$$

as shown in the appendix J. One notes that the matrix (in square brackets) on the left hand side is nothing else than the inverse of the density response function, i.e. $\chi^{-1}(\mathbf{r}, \mathbf{r}'; \omega)$, expressed in the basis of the product of Kohn-Sham orbitals $\Phi_{ml}(\mathbf{r})$. Since $\chi(\mathbf{r}, \mathbf{r}'; \omega)$ has poles at the exact excitation frequencies Ω , the aforementioned matrix is not invertible at these frequencies. We thus have to solve the same eigenvalue problem as it is given by Eq.(5.65) to determine Ω . To underpin this argument, inspection of Eq.(5.70) reveals an inhomogeneous set of equation. It has a complete solution that consists of the solution to the homogeneous equation plus a particular solution to the inhomogeneous equation. In particular, Eq.(5.70) resembles the equation of motion of a system of forced oscillators known from classical mechanics [see e.g. [124]]. The solution of the unforced system, when $V_{\text{ext}} = 0$ describes the free oscillation of the system or its eigenmodes with eigenfrequencies Ω that are of interest. Hence, in the context of linear response theory the external potential is usually treated as a small perturbation that triggers the system at its eigenfrequencies (the resonance frequencies of the system). As it is further supposed to be switched on adiabatically, the system then oscillates in phase with the external potential $V_{\text{ext}}(\omega)$, which allows to describe the resonances of the system unambiguously. In the work of Casida [122, 123], the eigenvalue problem from Eq.(5.65) is also solved but re-expressed into a squared eigenvalue problem. Instead of solving the homogenous set of equation due to Eq.(5.70), the Casida approach solves for the real part of the density variation $\Re[\delta\rho(\omega)]$ from Eq.(5.70) and makes use of the explicit expression for the macroscopic polarizability $\alpha(\omega)$ that relates the induced dipol moment to the external field strength. From classical electrodynamics one knows that a weak applied external field acting on a medium causes a displacement of the internal charges. Assuming the medium to be charge-neutral from the outside, its total charge expanded into a multipol expansion, starts with the dipol moment term denoted as $\boldsymbol{\mu}$.⁹ Hence, the charge displacement leads to a induced dipol moment $\delta\boldsymbol{\mu}$. Due to the weakness of the external field,

⁹The contribution to the total charge Q due to the dipol moment is then given by $Q_{\text{dipol}} \equiv \boldsymbol{\mu} = \int d\mathbf{r}' \rho(\mathbf{r}') \mathbf{r}'$.

the polarization¹⁰ may be expanded into a series expansion in powers of the electric field [see e.g.[125]] and we may write

$$\delta\mu_\gamma(t) \equiv \mu_\gamma(t) - \mu_\gamma = \int dt' \alpha_{\gamma\beta}(t-t') E_\beta(t'), \quad (5.71)$$

where the indices γ and β denote the cartesian components of the corresponding vector in Eq.(5.71) and the polarizability $\alpha_{\gamma\beta}$ is a second rank tensor with $\gamma, \beta = x, y, z$. After a Fourier transformation of Eq.(5.71) to frequency space, the components of the macroscopic polarizability tensor are easily related to the applied external field components:

$$\alpha_{\gamma\beta}(\omega) = \frac{\delta\mu_\gamma(\omega)}{E_\beta(\omega)}. \quad (5.72)$$

On the other hand, the induced dipol moment is given by

$$\delta\mu_\gamma(\omega) = \sum_{m,l} \delta\rho_{ml}(\omega) \gamma_{lm}, \quad (5.73)$$

where the matrix elements are expressed in terms of the unperturbed Kohn-Sham orbitals. For the cartesian coordinate γ we thus have $\gamma_{lm} = \int d\mathbf{r}' \varphi_l(\mathbf{r}') \varphi_m^*(\mathbf{r}') \gamma$ and the corresponding expression for the density variation $\delta\rho_{ml}(\omega)$ is already given by Eq.(5.69). To proceed with the macroscopic polarization one notes first that due to the Eqs.(5.72) and (5.73) the corresponding matrix elements $\alpha_{\gamma\beta}(\omega)$ are given by

$$\alpha_{\gamma\beta}(\omega) = \sum_{m,l} \frac{\Re[\delta\rho_{ml}(\omega)] \gamma_{lm}}{E_\beta(\omega)}. \quad (5.74)$$

Hereby, we take into account only the real part of the density variation, as the density itself is real valued. What remains is to solve for the real part of the density variation from Eq.(5.70). As shown in previous publications[122, 103], this is obtained by a suitable unitary transformation that finally yields

$$\Re[\delta\rho_{ml}(\omega)] = [\mathbf{A}(\omega) - \mathbf{B}(\omega)]^{\frac{1}{2}} [\mathbf{C}(\omega) - \omega^2]^{-1} [\mathbf{A}(\omega) - \mathbf{B}(\omega)]^{\frac{1}{2}} \Re[V_{\text{ext}}(\omega)]. \quad (5.75)$$

The matrix $\mathbf{C}(\omega)$ is thereby defined as

$$\mathbf{C}(\omega) = [\mathbf{A}(\omega) - \mathbf{B}(\omega)]^{\frac{1}{2}} [\mathbf{A}(\omega) + \mathbf{B}(\omega)] [\mathbf{A}(\omega) - \mathbf{B}(\omega)]^{\frac{1}{2}} \quad (5.76)$$

and obeys the squared generalized eigenvalue problem

$$\mathbf{C}(\omega)\mathbf{Z} = \Omega^2\mathbf{Z} \quad \text{with} \quad \mathbf{Z} = [\mathbf{A}(\omega) - \mathbf{B}(\omega)]^{\frac{1}{2}} [\mathbf{X} - \mathbf{Y}]. \quad (5.77)$$

The vectors $\mathbf{X}$ and $\mathbf{Y}$ can be identified with $\delta\boldsymbol{\rho}(\omega)$ and $\delta\boldsymbol{\rho}^*(\omega)$, respectively and form a super-vector that eventually solves the homogenous eigenvalue problem of Eq.(5.70). We will show

¹⁰The polarization is usually called as the dipol density and is related to the dipol moment by $\mathbf{P}(\mathbf{r}) = \boldsymbol{\mu}\delta(\mathbf{r})$.

in chapter 7 how to generate the quadratic eigenvalue problem due to Eq.(5.77) in more detail. Finally, the combination of Eq.(5.74) and Eq.(5.75) allows to solve for the macroscopic polarizability, if we assume furthermore a spatially homogeneous¹¹ electric field $\mathbf{E}$ as an external perturbation. Thus, the external potential may be written as $V_{\text{ext}} = \hat{\gamma}E_{\gamma}$ ¹², while the tensor components of the macroscopic polarizability become

$$\alpha_{\gamma\beta}(\omega) = 2\gamma^{\dagger} [\mathbf{A}(\omega) - \mathbf{B}(\omega)]^{\frac{1}{2}} [\mathbf{C}(\omega) - \omega^2]^{-1} [\mathbf{A}(\omega) - \mathbf{B}(\omega)]^{\frac{1}{2}} \beta^{13}. \quad (5.78)$$

What remains is to solve the inverse matrix $[\mathbf{C}(\omega) - \omega^2]^{-1}$, that can be done in the same manner as we have demonstrated for the excitonic operator in section 4.1.7. The underlying Green's function operator $\mathcal{G}$ is now defined by the relation $[\mathbf{C}(\omega) - \omega^2] \mathcal{G} = \mathbb{1}$. Hence, by use of the resolvent for $\mathbf{C}$ we find[103, 122]

$$[\mathbf{C}(\omega) - \omega^2]^{-1} = \sum_n \frac{\mathbf{Z}_n \mathbf{Z}_n^{\dagger} R_n}{\Omega_n^2 - \omega^2}. \quad (5.79)$$

The frequency dependence of the matrix $\mathbf{C}(\omega)$ turns the squared eigenvalue problem into an anti-Hermitian problem and similar for the generalized homogeneous eigenvalue problem due to Eq.(5.70)[103]. This is usually cured, by choosing a static exchange-correlation kernel $f_{\text{xc}}(\omega = 0)$, which results from the adiabatic approximation. In this particular case, the eigenvalue problem in Eq.(5.77) becomes Hermitian and may be solved explicitly yielding pure real eigenvalues Ω^2 . Furthermore, the normalization factor R_n in Eq.(5.79) then becomes 1. In particular, from the macroscopic polarizability tensor one can conclude to the macroscopic dielectric tensor $\epsilon_{\gamma\beta,\text{M}}$ through the relation[126]

$$\epsilon_{\gamma\beta,\text{M}}(\omega) = 1 - 4\pi\alpha_{\gamma\beta}(\omega). \quad (5.80)$$

In particular, the longitudinal component of the dielectric tensor $\epsilon_{\gamma\beta,\text{M}}(\omega)$, given by Eq.(4.95), is the algebraic equivalent to Eq.(4.63).

5.4.3. Approximations of the xc-kernel f_{xc}

Local density approximation and related issues

The general problem with the exchange-correlation kernel is that it cannot be derived as the second functional derivative due to the contradiction of causal and symmetry requirements as discussed in section 5.2. Since the $f_{\text{xc}}[\rho]$ kernel itself is given by a functional derivative one concludes that the time-dependent $V_{\text{xc}}[\rho](\mathbf{r}, t)$ cannot be given as a functional derivative [109]. This issue can be circumvented by imposing the adiabatic approximation to $f_{\text{xc}}[\rho](\mathbf{r}t, \mathbf{r}'t')$ a priori, thus approximating the time-dependent xc-potential with a static ground state xc-potential. The latter one then is given explicitly as a functional derivate with respect to the density as

¹¹An homogeneous field captures the long wave length limit, i.e. the $\mathbf{q} = 0$ component of the corresponding Fourier coefficient $\mathbf{E}(\mathbf{q})$.

¹²The vector $\hat{\gamma}$ denotes the unit vector along a cartesian direction.

¹³Different to the unit vector $\hat{\gamma}$ the vectors γ and β are expressed within the basis of the product of unperturbed Kohn-Sham orbitals, i.e. $\Phi_{ml}(\mathbf{r})$ with matrix elements as denoted in the text.

known from static density functional theory. On the other hand the xc-kernel is additionally non-local with respect to the spatial arguments and has a functional dependence on the entire density $\rho(\mathbf{r})$. As a straightforward approximation it suggests itself to approximate $f_{xc}[\rho]$ by the homogeneous counterpart $f_{xc}^{\text{hom,adiab}}(\rho)$ that is explicitly known for a homogeneous density $\rho(\mathbf{r}) = \text{const}$. Applied to the actual inhomogeneous density the corresponding xc-kernel depends then only upon the spatial distance, i.e. $f_{xc}^{\text{hom,adiab}}(\rho(\mathbf{r}); |\mathbf{r} - \mathbf{r}'|)$, thus we have a local density approximation upon the density dependence[109]. However, in this context it is not obvious at which spatial point the density needs to be evaluated along the range of $f_{xc}^{\text{hom}}(\rho(\mathbf{r}); |\mathbf{r} - \mathbf{r}'|)$. Assuming that not only the density $\rho(\mathbf{r})$ but also its variation varies slowly over the distance $|\mathbf{r} - \mathbf{r}'|$ one might impose a kind of *double* local density approximation [127] on the xc-kernel. As a result the adiabatic local density approximation[127] is obtained

$$f_{xc}^{\text{ALDA}}[\rho](\mathbf{r}t, \mathbf{r}'t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}') \left. \frac{d^2 e_{xc}^{\text{hom}}(\rho)}{d\rho} \right|_{\rho=\rho_{\text{gs}}(\mathbf{r})} \quad (5.81)$$

where e_{xc}^{hom} is the exchange-correlation energy per particle of the homogeneous electron gas. Moreover, the Fourier analysis of $f_{xc}^{\text{hom}}(\rho(\mathbf{r}); |\mathbf{r} - \mathbf{r}'|)$ with respect to $|\mathbf{r} - \mathbf{r}'|$ reveals that within the adiabatic local density approximation the xc-kernel is also independent of the wave vector since

$$f_{xc}^{\text{ALDA}}(q) = \lim_{q \rightarrow 0} f_{xc}^{\text{hom,adiab}}(q).^{14} \quad (5.82)$$

Therefore, as the xc-kernel within ALDA is q -independent, it cannot have a divergence that goes with $1/q^2$ for vanishing wave vector when $q \rightarrow 0$. This particular divergence is important to capture excitonic effects in extended systems with respect to the calculation of optical absorption spectra of extended systems[128]. The physical concept behind this missing divergence is that within the local density approximation the correct long range behaviour of $f_{xc}(\mathbf{r}, \mathbf{r}')$, if evaluated at the actual inhomogeneous density, is not captured. If one wishes to include this long range behaviour, the xc-kernel needs to be in general frequency dependent and thus requires a non-adiabatic formulation, i.e. $f_{xc}(\omega)$. This is a consequence of the zero-force theorem for the xc-kernel [103] that implies a strong non-local character for $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$. In that context one is faced with the ultra-nonlocality problem, i.e. the non-local xc-kernel is additionally dependent on the time difference $t - t'$. An explicit expression for a dynamic and long ranged xc-kernel has been given e.g. by Nazarov [129] for weakly inhomogeneous densities and has the desired $1/q^2$ dependence in the limit $\mathbf{q} \rightarrow 0$.

¹⁴For the homogeneous electron gas, the $\mathbf{q}$ -dependence reduces to the absolute length of the wave vector $q = |\mathbf{q}|$, since there is no dependence on the direction of $\mathbf{q}$ in the uniform electron gas.

6. The computational approach

The main purpose of this work concerns the calculation of the optical spectra of bulk systems and molecules. As we have seen in the previous sections, one major contribution to the calculation of the density response function are the energies of independent (quasi)particles.¹ In the case of optical transition energies, we exclusively deal with transitions from the valence band into the unoccupied manifold. The reason is due to the small excitation energies compared to the strongly bound core states whose inclusion to the optical spectrum can be safely neglected. Hence, an accurate description of the involved valence states or the corresponding orbital wave functions is required.

6.1. Pseudopotentials

Their numerical description, however, proves to be difficult. In a crystal with periodic boundary conditions, the Bloch states already imply a representation in terms of plane waves. Such a basis set has the advantage to be a complete set and thus allows for an exact representation. On the other hand, the all-electron valence orbitals show distinct oscillations close to the nucleus where the core electrons are localized. These oscillations are owing to the necessary orthogonalization of the valence states with respect to the core states[130]. This can be reasoned since the tightly bound core electrons repel the valence electrons much stronger in the atomic core neighborhood and thus give rise to a kinetic energy contribution. In a plane wave representation this requires a high number of Fourier components and renders the numerical description difficult. Therefore it would be desirable to circumvent this rapid oscillations near the nucleus and construct a valence state that behaves smoothly within the atomic region. A first approach in this direction was the method of *orthogonalized plane waves*[131] where a single plane wave was orthogonalized to all atomic core orbitals. The resulting (pseudo) valence state indeed has a less pronounced oscillation close to the nucleus at the cost of non-orthonormality. The resulting Hamiltonian transform into a pseudo-Hamiltonian that also contains a corresponding pseudopotential. The latter one, however, still depends on the atomic core states and thus cannot generate an atomic potential that could be expanded by a moderate number of plane waves. In order to get rid of the core states at all, ionic pseudopotential have been 'invented' with the task to replace the potential of the nucleus and the core electrons, and hence reduce the many-particle problem to a problem of only interacting valence electrons. The construction of a suitable pseudopotential interlaces the demand of transferability and smoothness. While the first point concerns the universal application of the pseudo potential within different atomic environments, the second

¹Within the framework of TDDFT, we are interested in the Kohn-Sham energies of the reference system of independent particles, while the solution of the BSE for the density correlation function requires the independent quasiparticle energies.

point refers to its spatial extend. The more localized it is the more Fourier coefficient are required in a plane wave description but localization improves the transferability. Usually, a cut-off radius r_c is introduced to set a boundary at which the real and the pseudo potential coincide and the cut-off radius might be regarded as a variable that controls the 'hardness' of the PP. Moreover, the cut-off radius separates the entire atomic environment into two parts. The first part is an interstitial region where the PP equals the real atomic potential (nucleus and core electrons) while in the second part close to the nucleus the potentials differ. For the generation of the PP, the corresponding free atom is taken as a reference system for which all-electron orbitals and energies are obtained (e.g. within DFT) from the solution of the radial Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m_e} \left[\frac{d^2}{dr^2} - \frac{l(l+1)}{2r^2} \right] + V_{\text{eff}}(r) - \varepsilon_{n,l} \right\} \phi_{n,l}(r) = 0. \quad (6.1)$$

Hereby, the effective potential comprises (in the case of a DFT approach) the external potential, as well as the Hartree potential and the exchange-correlation potential. The index n, l denote the main quantum number and the angular quantum number, respectively. The general approach to generate the pseudopotential consists of either a basis set expansion [132, 133] or parametric ansatz [134, 135] with the main objective to match the real potential outside the cut-off radius and giving a smooth continuation inside the core region. On the other hand, a numerical approximation of the pseudo wave function seems to be more appropriate, since it is connected with certain boundary conditions at the cut-off radius. Then from a given pseudo wave function $\tilde{\phi}_{n,l}$, the corresponding effective PP is obtained by inversion of the radial Schrödinger equation (6.1). In this procedure, the orbital pseudo energy $\tilde{\varepsilon}$ is usually set to the eigenenergy of the bound states $\phi_{n,l}$ of the all-electron calculation. As a result, the atomic pseudopotential is gained by subtracting the Hartree and the exchange-correlation part from the effective PP ('unscreening'). As the pseudo orbitals obey a corresponding Schrödinger equation of the form

$$\hat{H} |\tilde{\phi}_i\rangle = \tilde{\varepsilon}_i |\tilde{\phi}_i\rangle \quad (6.2)$$

they satisfy the orthonormality condition

$$\langle \tilde{\phi}_i | \tilde{\phi}_j \rangle = \delta_{ij}. \quad (6.3)$$

Pseudopotentials that reproduce orthonormal valence orbitals are called *norm-conserving* and satisfy several conditions. Among them is that the integrated charge Q_l evaluated on a radial grid is the same for the radial pseudo orbital $\tilde{\phi}_l(r)$ and for the corresponding all-electron orbital $\phi_l(r)$, i.e.

$$Q_l = \int_0^{r_c} dr \phi_l(r) = \int_0^{r_c} dr \tilde{\phi}_l(r). \quad (6.4)$$

This condition, however, might hamper to construct PP that are required to be as smooth as possible. The method of ultrasoft pseudopotentials [136] hence gives up this constraint, but needs to introduce the correct norm by introducing augmentation or depletion charges. The price to be paid is the non-orthonormality of the corresponding pseudo orbital $\tilde{\phi}^{\text{US}}$ that obeys a generalized

eigenvalue problem

$$\hat{H}^{\text{US}} |\tilde{\phi}_i^{\text{US}}\rangle = \tilde{\varepsilon}_i \tilde{S} |\tilde{\phi}_i^{\text{US}}\rangle \quad (6.5)$$

where $\tilde{S}$ is the overlap operator. As the only condition for the valence orbital $\tilde{\phi}_i^{\text{US}}(r)$ is to match the all-electron orbital at the boundary r_c its construction becomes more flexible. Due to the construction idea of the pseudopotentials, information about the core electrons gets lost that introduces errors e.g. for total energies in the order of about 10^{-2}eV . More importantly, is the fact that by the PP method the corresponding full all-electron wave function (for valence and core states) is not provided. Hence there is no access to the true physical quantities such as all-electron charge densities and other core related properties.

6.2. The projected augmented wave method

The electronic structure calculations that have been performed in this work are based on the Vienna Ab-initio package (VASP). It makes use of the PAW method that comprises the essential ideas of the ultrasoft pseudopotential method[136] and of the linearized augmented wave method[137]. It became popular as it gives access to the all-electron wave function by a linear transformation and formally includes the core states within the frozen core approximation. I follow closely the Refs.[138, 139, 140]. The key point within the PAW method is to find a proper linear transformation between the full all-electron wave function Ψ and the corresponding pseudo wave function $\tilde{\Psi}$ tied with the linear operator $\mathcal{T}$

$$|\Psi\rangle = \mathcal{T} |\tilde{\Psi}\rangle. \quad (6.6)$$

While both wave functions Ψ and $\tilde{\Psi}$ shall coincide outside the core region, defined by a cut-off radius, the operator $\mathcal{T}$ needs to recast the nodal structure of the all-electron wave function close to the nucleus from the pseudo wave function. In order to regain the oscillating character of the AE wave function, the contribution of the smooth function due to the PP approach has to be replaced by an atomic-like wave function obtained from the radial Schrödinger equation (6.1). Hence, a reasonable form of the transformation reads as a sum of the identity plus a local term specific for each atomic site R :

$$\mathcal{T} = \mathbf{1} + \sum_R \mathcal{T}_R. \quad (6.7)$$

The effect of the transformation operator becomes more obvious if the pseudo wave function is expressed as a linear combination in terms of the complete basis set of the pseudo partial waves $\tilde{\phi}$ inside the core region Ω_R

$$|\tilde{\Psi}\rangle = \sum_j c_j |\tilde{\phi}_j\rangle \quad \text{within } \Omega_R \quad (6.8)$$

and similar for the AE wave function

$$|\Psi\rangle = \sum_j c_j |\phi_j\rangle \quad \text{within } \Omega_R. \quad (6.9)$$

Due to Eq.(6.6) the action of the local part $\mathcal{T}_R$ is thus given by

$$\mathcal{T}_R |\tilde{\Psi}\rangle = \sum_j \left(|\phi_j\rangle - |\tilde{\phi}_j\rangle \right) c_j \quad \text{within } \Omega_R, \quad (6.10)$$

where the index j collates the set of quantum numbers $\{m, l\}$ at a specific site R . The yet unknown expansion coefficients c_j are defined through the projector functions $\tilde{p}_j$

$$c_j = \langle \tilde{p}_j | \tilde{\Psi} \rangle \quad (6.11)$$

that act only locally in the core region. If one substitutes Eq.(6.11) into Eq.(6.8) the pseudo partial wave function and the projector function have to fulfill the closure relation $\sum_j |\tilde{\phi}_j\rangle \langle \tilde{p}_j| = \mathbf{1}$. Moreover, both set of functions constitute a bi-orthogonal system with the orthogonality relation

$$\langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij}. \quad (6.12)$$

As a result the full transformation operator $\mathcal{T}$ becomes

$$\mathcal{T} = \mathbf{1} + \sum_{j'} \left(|\phi_{j'}\rangle - |\tilde{\phi}_{j'}\rangle \right) \langle \tilde{p}_{j'}|, \quad (6.13)$$

whereas the index j' now includes also the summation over all atomic sites. Outside the core region the operator is simply the unity operator, which means that AE and pseudo wave functions are the same. This region is usually denoted as the interstitial region. As the AE wave function approaches the nucleus it starts oscillating, which is accounted for by the summation over the partial AE waves. However, the correct behaviour of the AE wave function is only obtained if the contribution of the smoothly varying pseudo partial waves are subtracted. Hereby, the projector $\tilde{p}_j$ probes the local character of the pseudo wave function $\tilde{\Psi}$ inside the core region and thus determines the fraction of $\tilde{\phi}_j$ that needs to be subtracted through the coefficient c_j [Eq.(6.12)]. Additionally, within the PAW method the AE partial waves, obtained from the radial Schrödinger equation (6.1) are restricted to the valence orbitals and are hence consistently orthogonal to the core states of the atom. The latter one are treated independently to the valence orbitals. They usually do not overlap with adjacent atomic core states, e.g. in a solid. Therefore, core states from an isolated atom are kept frozen when they are imported into the solid framework (frozen core approximation). The split up of the AE wave function is again shown schematically in Fig. 6.1 and illustrates the augmentation procedure. Within the interstitial region, the AE wave

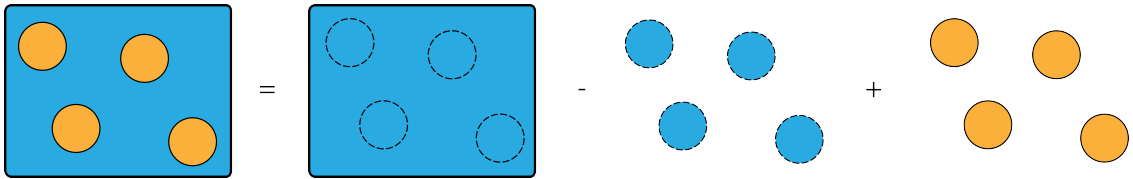


Figure 6.1.: Graphical representation of the all-electron wave function Ψ from Eq.(6.14). The circles associates the one-center regions.

function is expressed by a moderate number of plane waves. The core or augmentation region is *enriched* by the difference term $(|\phi_j\rangle - |\tilde{\phi}_j\rangle)c_j$ and the set of basis functions of plane waves to express the AE wave function, is extended by the function $h(\mathbf{r}) \equiv \sum_j (\phi_j(\mathbf{r}) - \tilde{\phi}_j(\mathbf{r}))c_j$. Due to the transformation operator $\mathcal{T}$, the AE wave function can be decomposed into three different parts:

$$|\Psi\rangle = |\tilde{\Psi}\rangle + \underbrace{\sum_{j'} |\phi_{j'}\rangle \langle \tilde{p}_{j'} | \tilde{\Psi}\rangle}_{\sum_R |\Psi_R^1\rangle} - \underbrace{\sum_{j'} |\tilde{\phi}_{j'}\rangle \langle \tilde{p}_{j'} | \tilde{\Psi}\rangle}_{\sum_R |\tilde{\Psi}_R^1\rangle}. \quad (6.14)$$

The first term describes the smooth part in the interstitial region and is numerically calculated on a regular real space grid. The second term $|\Psi_R^1\rangle$ denotes the one-center expansion of the true AE wave function within the core region Ω_R , while the third term $|\tilde{\Psi}_R^1\rangle$ is the corresponding one-center expansion of the smooth pseudo wave function within Ω_R . As the partial waves ϕ_j vary rapidly close to the nucleus, the one-center expansions are calculated on a radial grid. Moreover, in practical applications the one-center expansion due to Eq.(6.9) is not strictly fulfilled and the expansion is truncated. In that case the missing expansion terms are substituted by plane waves and lead to a rapid convergence of the one-center expansion [140].

Expectation values and overlap operator

Similar to the separation of the AE wave function due to Eq.(6.14) one finds a similar form for the real space density or any other local operators. The density plays, however, an essential role, as it is required for the calculation of the total energy. It is calculated from the expectation value of the real space density operator $|\mathbf{r}\rangle \langle \mathbf{r}|$ and hence given by

$$\rho(\mathbf{r}) = \langle \Psi | \mathbf{r} \rangle \langle \mathbf{r} | \Psi \rangle \quad (6.15)$$

and further with the aid of Eq.(6.14) one obtains

$$\rho(\mathbf{r}) = \left\langle \tilde{\Psi} + \sum_R \left(\Psi_R^1 - \tilde{\Psi}_R^1 \right) \middle| \mathbf{r} \right\rangle \left\langle \mathbf{r} \middle| \tilde{\Psi} + \sum_{R'} \left(\Psi_{R'}^1 - \tilde{\Psi}_{R'}^1 \right) \right\rangle. \quad (6.16)$$

The resulting contributions may be grouped into one non-vanishing term

$$\langle \tilde{\Psi} | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi} \rangle + \sum_R \left(\langle \Psi_R^1 | \mathbf{r} \rangle \langle \mathbf{r} | \Psi_R^1 \rangle - \langle \tilde{\Psi}_R^1 | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi}_R^1 \rangle \right) \quad (6.17)$$

and two vanishing contributions

$$+ \sum_R \left(\langle \Psi_R^1 - \tilde{\Psi}_R^1 | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi} - \tilde{\Psi}_R^1 \rangle + \langle \tilde{\Psi} - \tilde{\Psi}_R^1 | \mathbf{r} \rangle \langle \mathbf{r} | \Psi_R^1 - \tilde{\Psi}_R^1 \rangle \right) \quad (6.18)$$

$$+ \sum_{R \neq R'} \langle \Psi_R^1 - \tilde{\Psi}_R^1 | \mathbf{r} \rangle \langle \mathbf{r} | \Psi_{R'}^1 - \tilde{\Psi}_{R'}^1 \rangle \quad (6.19)$$

for the local real space density operator. Concerning the term $\Psi_R^1 - \tilde{\Psi}_R^1$, it obviously vanishes outside the core region Ω_R since the AE partial waves and pseudo partial waves coincide in the

interstitial region. On the other hand, the expression $\tilde{\Psi} - \tilde{\Psi}_R^1$ becomes zero inside the core region as the pseudo wave function is given by the one-center expansion (6.8). Therefore, no matter which spatial region is considered the expression in Eq.(6.18) vanishes at any point. A similar argument also holds for Eq.(6.19). Since the one-center terms are restricted to one specific atomic site they cannot become non-zero anywhere else outside a particular core region Σ_R . Hence, the real space density contains a smooth pseudo part and two one-site expressions:

$$\begin{aligned} \rho(\mathbf{r}) = & \underbrace{\sum_p f_p \langle \tilde{\Psi}_p | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\Psi}_p \rangle}_{\tilde{\rho}(r)} \\ & + \underbrace{\sum_{p,i',j'} f_p \langle \tilde{\Psi}_p | \tilde{p}_{i'} \rangle \langle \phi_{i'} | \mathbf{r} \rangle \langle \mathbf{r} | \phi_{j'} \rangle \langle \tilde{p}_{j'} | \tilde{\Psi}_p \rangle}_{\rho^1(r)} \\ & - \underbrace{\sum_{p,i',j'} f_p \langle \tilde{\Psi}_p | \tilde{p}_{i'} \rangle \langle \tilde{\phi}_{i'} | \mathbf{r} \rangle \langle \mathbf{r} | \tilde{\phi}_{j'} \rangle \langle \tilde{p}_{j'} | \tilde{\Psi}_p \rangle}_{\tilde{\rho}^1(\mathbf{r})}, \end{aligned} \quad (6.20)$$

where the Fermi function is denoted as f_p . The core states have not been considered yet. However, they can be decomposed similar to the valence states [see Eq.(6.14)] as

$$|\Psi^c\rangle = |\tilde{\Psi}^c\rangle + |\phi^c\rangle - |\tilde{\phi}^c\rangle, \quad (6.21)$$

and give rise to core state densities $\tilde{\rho}_c(r)$, $\tilde{\rho}_c^1(r)$ and $\rho_c^1(r)$ similar to the valence states. However, the one-site density matrix $D_{i,j}$ defined for the valence states [compare Eq.(6.20)]

$$D_{i,j} = \sum_p f_p \langle \tilde{\Psi}_p | \tilde{p}_{i'} \rangle \langle \tilde{p}_{j'} | \tilde{\Psi}_p \rangle \quad (6.22)$$

becomes 1 in the case of core states. Hence, to obtain the full real space density, the corresponding core densities can be added to the valence densities separately for the smooth terms and the one-center terms. Within the PAW method, another charge density is usually introduced, which is known as the compensation charge $\hat{\rho}$. This becomes important for the calculation of the total energy, in particular, the Hartree term. The compensation charge needs to be added to the pseudo density $\tilde{\rho}$ as well as to the corresponding one-center term $\tilde{\rho}^1$, whenever the integrated charge of the pseudo wave function and the AE wave function inside the core region (augmentation region) yields non-vanishing contributions. The resulting augmentation charge is hence given by

$$\rho^{\text{aug}}(\mathbf{r}) = \rho^1(\mathbf{r}) - \tilde{\rho}^1(\mathbf{r}) = \sum_{(i,j) \in R} D_{ij} Q_{ij} \quad \text{with} \quad Q_{ij} = \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) - \tilde{\phi}_i^*(\mathbf{r}) \tilde{\phi}_j(\mathbf{r}) \quad (6.23)$$

and yields a net charge density that interacts with charges outside the augmentation region [138]. This might be suppressed by a compensation charge that has the same multipoles as the augmentation charge density. From classical electrodynamics [see e.g.[141]] multipoles of a charge distribution are expressed by spherical harmonics Y_L . Hence, the augmentation charge

reads

$$q_{ij,L} = \int_{\Omega_R} d\mathbf{r} Q_{ij} |\mathbf{r} - \mathbf{R}| Y_L^*(\mathbf{r} - \mathbf{R}) \quad (6.24)$$

and allows to calculate the corresponding compensation charge density in the following manner [142]

$$\hat{\rho}(\mathbf{r}) = \sum_{(i,j),L} D_{ij} q_{ij,L} g_l(|\mathbf{r} - \mathbf{R}|) Y_L(|\mathbf{r} - \mathbf{R}|) \quad (6.25)$$

with the function g_l that is expressed in terms of Bessel functions in VASP. It confines the compensation charge into a spherical region where the AE and pseudo charge coincides at the boundary [142]. The resulting energy contributions to the total energy have been discussed e.g. in [138] and [142]. To conclude this section, the overlap operator shall be given. It is readily obtained from the derivation of the real space charge density demonstrated in Eq.(6.20). Substituting the real space density operator $|\mathbf{r}\rangle\langle\mathbf{r}|$ by the unity operator $\int d\mathbf{r} |\mathbf{r}\rangle\langle\mathbf{r}| = \mathbf{1}$ one obtains

$$\tilde{S} = \mathbf{1} + \sum_{i',j'} |\tilde{p}_{i'}\rangle \left(\langle\phi_i|\phi_j\rangle - \langle\tilde{\phi}_i|\tilde{\phi}_j\rangle \right) \langle\tilde{p}_j|. \quad (6.26)$$

Due to the linear transformation operator, the Schrödinger equation in the PAW method becomes a generalized eigenvalue problem because of the overlap operator. To give evidence, one notes that the transformation due to the operator $\mathcal{T}$ is a unitary transformation as it leaves the eigenvalue of the expectation value unchanged, i.e.

$$E = \langle\Psi|\hat{H}|\Psi\rangle = \langle\tilde{\Psi}|\hat{\mathcal{T}}^\dagger H \hat{\mathcal{T}}|\tilde{\Psi}\rangle = \langle\tilde{\Psi}|\hat{\tilde{H}}|\tilde{\Psi}\rangle. \quad (6.27)$$

With the Rayleigh-Ritz method the pseudo part of the expectation value can be varied with respect to pseudo function $\tilde{\Psi}$. If the latter one is a ground state pseudo wave function, the variation δE vanishes and the pseudo Schrödinger equation is obtained

$$\left(\mathcal{T}^\dagger \hat{H} - \mathcal{T}^\dagger E \right) \mathcal{T} |\tilde{\Psi}\rangle = 0 \iff \hat{\tilde{H}} |\tilde{\Psi}\rangle = E \mathcal{T}^\dagger \mathcal{T} |\tilde{\Psi}\rangle = E \tilde{S} |\tilde{\Psi}\rangle \quad (6.28)$$

with the pseudo eigenstates satisfying the orthogonalization condition

$$\langle\tilde{\Psi}_i|\tilde{S}|\tilde{\Psi}_j\rangle = \delta_{ij}. \quad (6.29)$$

7. Beyond the Tamm-Dancoff approximation for extended systems using exact diagonalization*

The study of optical properties of condensed matter and molecular systems is a field of growing interest, not least because of the emerging importance of renewable energies, and the requirement to accurately predict the optical properties of novel composite materials and nanostructures. Time-dependent density functional theory (TDDFT) has certainly been the most widely used approach to date, although it is not without problems. In TDDFT, an effective two-point Dyson like equation relates the density response function of the non-interacting Kohn-Sham system $\chi_0(\mathbf{r}, \mathbf{r}', t - t')$ to the (linear) density response function of the interacting system $\chi^{\text{TD}}(\mathbf{r}, \mathbf{r}', t - t')$: $\chi^{\text{TD}} = \chi_0 + \chi_0(v + f_{\text{xc}})\chi^{\text{TD}}$.[\[143\]](#) The "interaction" terms are described by the Coulomb kernel v and the exchange-correlation kernel f_{xc} . Unfortunately though, the interaction kernel does not allow for a systematic improvable expansion of the microscopic particle-particle interaction as would be the case e.g. for Green's function methods. Furthermore or rather resultantly, only few 2-point kernels, $f_{\text{xc}}(\mathbf{r}, \mathbf{r}', t - t')$, yield a satisfactory description of excitonic effects.[\[144, 145\]](#) Among them the most successful approximate kernels are the nano-quanta kernel,[\[146, 147, 148\]](#) the boot strap kernel of Sharma,[\[149\]](#) and kernels based on the jellium with a gap.[\[150\]](#) The nano-quanta kernel requires one to explicitly calculate the two-electron four-orbital integrals making it almost as expensive as the methods discussed below, whereas the latter two are yet not satisfactorily derived from first principles and fail to describe bound excitons accurately.[\[149\]](#)

Alternative descriptions rely on the so called Bethe-Salpeter equation. After some manipulation, the conventional Bethe-Salpeter equation— known from nuclear theory— can be cast, into a Dyson like equation

$$P = P_0 + P_0 I P,$$

where $P(1, 2, 3, 4)$ is the four-point time-ordered polarization propagator and I denotes the interaction kernel,[\[151\]](#) and we use the common notation for space and time points $1 = (\mathbf{r}_1, t_1)$. This equation resembles the response equation for χ^{TD} from TDDFT, where P can be regarded to be a generalized linear density matrix response function to a non-local perturbation [c.f. Eq. (63) in Ref. [\[152\]](#)].

Obviously manipulation of such 4-point quantities is much more involved than the simpler TDDFT 2-point quantities. In practice, the polarization propagator $P(1, 2, 3, 4)$ is expressed in a suitable two-orbital basis made up by all relevant combinations of electron and hole pairs. Furthermore, the electron-hole interaction kernel I is approximated by the Coulomb kernel v and a static (or more correctly instantaneous) screened interaction W . This static approximation

*Based on: T. Sander, E. Maggio and G. Kresse, Beyond the Tamm-Dancoff approximation for extended systems using exact diagonalization, [Physical Review B 92, 045209 \(2015\)](#).

is commonly applied to simplify the calculations. Inclusion of frequency dependent kernels is possible and e.g. important for the description of double excitations but computationally much more demanding[153, 154]. Also it has been shown that QP renormalization effects cancel against dynamical effects in the interaction kernel[153]. Hence, neglecting dynamical effects as done throughout this work is expected to yield accurate results.

The excitation energies are determined by calculating the resolvent of the polarization propagator. This usually requires the diagonalization of a large matrix, where the matrix dimension equals the number of occupied times the number of unoccupied states. Formally, the solution of this equation is then entirely equivalent to solving the so called "Casida" equation for time dependent DFT and time dependent Hartree-Fock.[155] For hybrid functionals, the only difference is that, in Casida's equation, the screened interaction W between electrons and holes is replaced by the Coulomb kernel v "screened" by the mixing parameter α . The mixing parameter α determines how much of the non-local exchange is included (in most cases $\alpha = 1/4$).

In addition to the static approximation $W(t, t') = W \delta(t, t')$, which is exactly observed for hybrid functionals, since the Coulomb kernel there is per construction instantaneous, a further approximation is commonly applied. To solve the BSE/Casida equation, the response functions (be it the 2-point or 4-point variants) are usually Fourier transformed to frequency space, where they are symmetric $\Re\chi(\omega) = \Re\chi(-\omega)$. In principle, terms between positive and negative frequency branches exist, describing the annihilation of two electron-hole pairs against each other, or the creation of two electron-hole pairs as a result of vacuum fluctuations. These diagrams and thus the interaction terms between the positive and negative frequency branch are often neglected, an approximation that is commonly referred to as Tamm-Dancoff approximation.[89, 90] Applying the Tamm-Dancoff approximation simplifies the computations tremendously, since the original full interaction matrix is not Hermitian and hence can not be solved via standard "canned" eigenvalue solvers. After decoupling the positive and negative frequency part, however, the polarization propagator becomes an Hermitian matrix, for which the resolvent can be easily calculated. It is common practice to consider only the resonant part of the polarization propagator, and we refer to it as Tamm-Dancoff approximation (TDA) within the manuscript. In the physics community, the full solution is usually determined by iterative solvers or time evolution algorithms,[156, 157] whereas in quantum chemistry, it is common to square the original problem.[158, 159] For solid state problems, the equivalent path has not yet been explored, essentially because the involved matrices are complex instead of symmetric, and it is not immediately obvious how to generalize the equations used in quantum chemistry to the complex case. By employing time inversion symmetry and mapping Bloch wave vectors $\mathbf{k}$ to $-\mathbf{k}$ in the negative frequency branch, we circumvent this problem and show that a similar approach as in quantum chemistry can be used. This allows to calculate all eigenvalues and eigenvectors of the 2-particle problem with an effort that is only about 2-3 times larger then for the Hermitian Tamm-Dancoff approximation. This opens a route to efficient and convenient calculations beyond Tamm-Dancoff with full access to all eigenvectors. We test the present approach for four simple systems, namely silicon (Si), carbon (C), lithium fluoride (LiF) and cyclic lithium fluoride dimer (Li_2F_2). We find essentially no (Si, C, LiF) or little (Li_2F_2) difference between the Tamm-Dancoff approximation

and the full approach, except for small errors in the static dielectric constant. However, the Tamm-Dancoff approximation clearly fails in the case of finite momentum transfer, and we give evidence for silicon by calculating the macroscopic dielectric function within TDA and beyond TDA at finite $\mathbf{q}$. Before discussing the present theoretical approach in detail, we present a concise derivation of, what is called the BSE/Casida equation. This includes a brief formal re-derivation and introduction of the squared problem. Our results are then presented in Sec. 7.7. The present calculations are based on an entirely parameter free description, in particular, the preceding GW calculations are state of the art. They are performed self-consistently in the Green's function G , using the quasiparticle (QP) GW method.[72] This allows to access how well state of the art procedures reproduce the experiment.

7.1. 4-point two particle propagator and Bethe-Salpeter equation

We consider a non-relativistic N -electron system with Hilbert space $\mathcal{H}^N = \wedge^N \mathcal{H}$, $\mathcal{H} = L^2$ and the standard Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$, where $\hat{H}_0$ corresponds to the sum of a kinetic term and a lattice periodic potential, whereas $\hat{V}$ denotes the Coulomb interaction. We assume Ψ_0 to be the non-degenerate ground-state of $\hat{H}$ with energy E_0^N . The 4-point propagator is defined[160, 161] as ($\hbar$ is set to 1 from now on)

$$i^2 G^4(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2, \mathbf{r}_3 t_3, \mathbf{r}_4 t_4) = \langle \Psi_0 | \mathcal{T} \left[\hat{\psi}(\mathbf{r}_1 t_1) \hat{\psi}(\mathbf{r}_2 t_2) \hat{\psi}^\dagger(\mathbf{r}_4 t_4) \hat{\psi}^\dagger(\mathbf{r}_3 t_3) \right] | \Psi_0 \rangle,$$

where $\mathcal{T}$ denotes the time ordering operator and $\hat{\psi}^{(\dagger)}(\mathbf{r}t)$ the field operators, the time-dependence being induced by the Heisenberg picture. The free 4-point propagator G_0^4 is defined analogously in terms of $\hat{H}_0$ and the corresponding ground-state Φ_0 (again supposed to be non-degenerate). The Wick theorem[160] for the free $2n$ -point Green's functions implies for the free 4-point propagator the equality

$$G_0^4(1, 2, 3, 4) = G_0(1, 3)G_0(2, 4) - G_0(1, 4)G_0(2, 3) \quad (7.1)$$

where $G_0(1, 2)$ corresponds to the free propagator. For the full 4-point propagator, one therefore usually makes the ansatz[161]

$$G^4(1, 2, 3, 4) = G(1, 3)G(2, 4) - G(1, 4)G(2, 3) - i \int d(5, 6, 7, 8) G(1, 5)G(2, 6)\Gamma_{\text{sc}}(5, 6, 7, 8)G(7, 3)G(8, 4), \quad (7.2)$$

where the so-called scattering amplitude Γ_{sc} is implicitly defined by this ansatz. $G(1, 2)$ denotes the Green's function defined by

$$i G(\mathbf{r}t, \mathbf{r}'t') = \langle \Psi_0 | \mathcal{T} \left[\hat{\psi}(\mathbf{r}t) \hat{\psi}^\dagger(\mathbf{r}'t') \right] | \Psi_0 \rangle. \quad (7.3)$$

A Feynman graph analysis shows that the scattering amplitude Γ_{sc} is the sum over all amputated, skeleton graphs that can be put between two electron-hole pairs. If one defines a sub-sum I which corresponds to all graphs that are irreducible in the electron-hole channel, then one necessarily

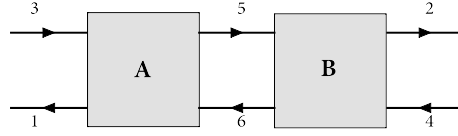


Figure 7.1.: Four-point formalism for matrix multiplication: $(AB)(1, 2, 3, 4) \stackrel{\text{def}}{=} \int d(5, 6) A(1, 5, 3, 6)B(6, 2, 5, 4)$. The index order is chosen to yield a convenient order in the two-electron four orbital integrals.

has

$$\Gamma_{\text{sc}} = I + iIGGI + i^2 IGGIGGI + \dots$$

implying

$$\Gamma_{\text{sc}}(1, 2, 3, 4) = I(1, 2, 3, 4) + i \int d(5, 6, 7, 8) I(1, 5, 3, 6)G(6, 7)G(8, 5)\Gamma_{\text{sc}}(7, 2, 8, 4). \quad (7.4)$$

This is the well-known Bethe-Salpeter equation for the scattering amplitude.[\[161\]](#)

7.2. Dyson like equation for two particle propagator

Introducing

$$L(1, 2, 3, 4) = G^4(1, 2, 3, 4) - G(1, 3)G(2, 4) \quad (7.5)$$

one shows easily by the Bethe-Salpeter equation for Γ that L fulfills a Dyson like equation of the form

$$L(1, 2, 3, 4) = L_0(1, 2, 3, 4) + i \int d(5, 6, 7, 8) L_0(1, 5, 3, 6)I(6, 7, 5, 8)L(8, 2, 7, 4), \quad (7.6)$$

where L_0 denotes the "free part" $-G(1, 4)G(2, 3)$. Inherent to the above 4-point matrix notation is the definition of the matrix product of 4-point quantities (see Fig.[\(7.1\)](#)) as

$$(AB)(1, 2, 3, 4) \stackrel{\text{def}}{=} \int d(5, 6) A(1, 5, 3, 6)B(6, 2, 5, 4). \quad (7.7)$$

As it has been stressed in Ref. [\[151\]](#), the simplest contribution to the interaction kernel I , which can be written as $I = V + \tilde{I}$, is the Coulomb interaction V . All other interaction diagrams are then obtained by approximating $\tilde{I}$, which means the inclusion of certain classes of Feynman diagrams. One class of diagrams are the particle-hole ladder diagrams that includes the so-called W -approximation of $\tilde{I}$, where W is the screened interaction known from Hedin's equations,[\[5\]](#)

but given in a four-point notation:

$$I(1, 2, 3, 4) \approx V(1, 2, 3, 4) - W(2, 1, 3, 4), \quad (7.8)$$

$$V(1, 2, 3, 4) := v(1, 4^+) \delta(4, 2^+) \delta(3, 1^+), \quad (7.9)$$

$$W(1, 2, 3, 4) := w(1, 4^+) \delta(4, 2^+) \delta(3, 1^+), \quad (7.10)$$

$$v(1, 4^+) := v(\mathbf{r}_1 - \mathbf{r}_4) \delta(t_1 - t_4^+),$$

$$w(1, 4^+) \approx \tilde{w}(\mathbf{r}_1, \mathbf{r}_4; \omega = 0) \delta(t_1 - t_4^+),$$

$$\delta(1, 2^+) = \delta(\mathbf{r}_1 - \mathbf{r}_1) \delta(t_1 - t_2^+).$$

The W -approximation is equivalent to the second iteration of Hedin's equations[5] with the approximation $\delta\Sigma/\delta G \approx W$ for the (irreducible) vertex function. This approximation further determines a Bethe-Salpeter Equation for the irreducible polarizability [c.f. Eq. (13.19c) in Ref. [5]], with W approximated in the random-phase approximation.

Notice that we assume here and in the following that both interactions are instantaneous and involve equal times $\delta(t_1 - t_4)\delta(t_4 - t_2)\delta(t_3 - t_1)$. This allows for a significant simplification. In particular, integrals of the form

$$\int d(5, 6, 7, 8) L_0(1, 5, 3, 6) I(6, 7, 5, 8) L(8, 2, 7, 4), \quad (7.11)$$

simplify to

$$\int dt' L_0(t_1, t', t_3, t'^+) (v - \tilde{w}) L(t', t_2, t'^+, t_4), \quad (7.12)$$

where the spatial indices have been dropped for notational simplicity, and the interaction I possesses no frequency dependence. The crucial point is that the time limits $t_3 \rightarrow t_1^+$ and $t_4 \rightarrow t_2^+$ can now be performed under the integral and Eq.(7.12) then reads

$$\int dt' L_0(t_1, t', t_1^+, t'^+) (v - \tilde{w}) L(t', t_2, t'^+, t_2^+). \quad (7.13)$$

This suggests that two time indices suffice to solve the BSE/Casida equation, as long as the interaction is entirely static or more precisely instantaneous.

7.3. Polarization propagator and density fluctuation response function

The 4-point propagator L is a computationally demanding object in that it depends on 4 arguments involving three time differences. As discussed above, the static approximation in terms of V [Eq.(7.9)] and W [Eq.(7.10)] allows one to reduce L to a quantity containing only the difference between two time arguments t_1 and t_2 and four spatial arguments. We will call this quantity henceforth the *time-reduced 4-point polarization propagator* or density fluctuation response function $P(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4; t_1 - t_2) = i L(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2, \mathbf{r}_3 t_1^+, \mathbf{r}_4 t_2^+)$ and stick consistently with the notation of previous publications[6, 162, 163] except for a factor i . The relation to the

(time-ordered) density-density fluctuation response function $\chi(1, 2)$ is obtained by contraction of spatial arguments, i.e. $\mathbf{r}_3 \rightarrow \mathbf{r}_1$ and $\mathbf{r}_4 \rightarrow \mathbf{r}_2$ or simply $\chi(1, 2) = P(1, 2, 1^+, 2^+)$:

$$\chi(\mathbf{r}t, \mathbf{r}'t') = -i \langle \Psi_0 | \mathcal{T} [\hat{\rho}_1(\mathbf{r}t) \hat{\rho}_1(\mathbf{r}'t')] | \Psi_0 \rangle \quad (7.14)$$

where the density fluctuation operator is defined as

$$\begin{aligned} \hat{\rho}_1(\mathbf{r}t) &= \hat{\psi}^\dagger(\mathbf{r}t) \hat{\psi}(\mathbf{r}t) - \langle \hat{\psi}^\dagger(\mathbf{r}t) \hat{\psi}(\mathbf{r}t) \rangle \\ &= \hat{\psi}^\dagger(\mathbf{r}t) \hat{\psi}(\mathbf{r}t) - \rho(\mathbf{r}), \end{aligned} \quad (7.15)$$

and $\rho(\mathbf{r})$ is the ground state density. The relation between P and χ can be straightforwardly shown using Eqs. (7.1, 7.3) and (7.5). The free 4-point polarization propagator P_0 is given in the frequency domain by a Lehmann representation, which reads

$$P_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = \sum_{\substack{a \in \text{unocc} \\ i \in \text{occ}}} \left[\frac{\varphi_a(\mathbf{r}_1) \varphi_i^*(\mathbf{r}_3) \varphi_i(\mathbf{r}_2) \varphi_a^*(\mathbf{r}_4)}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta} + \frac{\varphi_i(\mathbf{r}_1) \varphi_a^*(\mathbf{r}_3) \varphi_a(\mathbf{r}_2) \varphi_i^*(\mathbf{r}_4)}{-\omega - (\varepsilon_a - \varepsilon_i) + i\eta} \right]. \quad (7.16)$$

Here and in the following, we have disregarded the spin: for the non-magnetic case, a factor 2 must be added, whereas in the spin polarized case, an additional sum over spins needs to be included. The set of orbitals $\{\varphi_i(\mathbf{r})\}$ constitute an orthogonal basis and P_0 can be reformulated as

$$P_0(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \omega) = \sum_{k, l, m, n} \varphi_k(\mathbf{r}_1) \varphi_l^*(\mathbf{r}_3) \varphi_m(\mathbf{r}_2) \varphi_n^*(\mathbf{r}_4) P_0^{km}{}_{ln}(\omega), \quad (7.17)$$

where the sum goes over all states k, l, m, n . The matrix elements $P_0^{km}{}_{ln}(\omega)$ take the simple form

$$P_0^{km}{}_{ln}(\omega) = \frac{n_m(1 - n_k) - (1 - n_m)n_k}{\omega - (\varepsilon_k - \varepsilon_m) + \text{sgn}(\varepsilon_k - \varepsilon_m)i\eta} \delta_k^n \delta_l^m, \quad (7.18)$$

with the occupation numbers $n_{m,k} = n_i = \langle \Phi_0 | \hat{n}_i | \Phi_0 \rangle = \langle \Phi_0 | a_i^\dagger a_i | \Phi_0 \rangle$ referring to the non-interacting ground-state Φ_0 , i.e. $n_i = 1$ for $\varphi_i \in \{\varphi_{i_1}, \dots, \varphi_{i_N}\}$ where $\Phi_0 = 1/\sqrt{N!} \det(\varphi_{i_k}(\mathbf{r}_l))$ and $n_{k,m} = n_a = 0$ otherwise. We use an index notation that takes into account the different transformation behaviour under changes of the basis in the one-particle Hilbert space.[151] That means if one performs a change of basis in the one-particle Hilbert space given by a unitary matrix U , then the lower indices transform with U and the upper indices with U^* . For later purposes, we note that the matrix elements of the Coulomb potential are given (as usual) by

$$\begin{aligned} V_{kl}^{mn} &= \langle mn | V | kl \rangle = \langle \varphi_m \varphi_n | V | \varphi_k \varphi_l \rangle \\ &= \int d\mathbf{r} d\mathbf{r}' \varphi_m^*(\mathbf{r}) \varphi_n^*(\mathbf{r}') v(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}) \varphi_l(\mathbf{r}') \end{aligned} \quad (7.19)$$

and the exchange terms are correspondingly defined as:

$$\begin{aligned} W_{kl}^{mn} &= \langle nm | W | kl \rangle = \langle \varphi_n \varphi_m | W | \varphi_k \varphi_l \rangle \\ &= \int d\mathbf{r} d\mathbf{r}' \varphi_n^*(\mathbf{r}) \varphi_m^*(\mathbf{r}') w(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}) \varphi_l(\mathbf{r}'). \end{aligned} \quad (7.20)$$

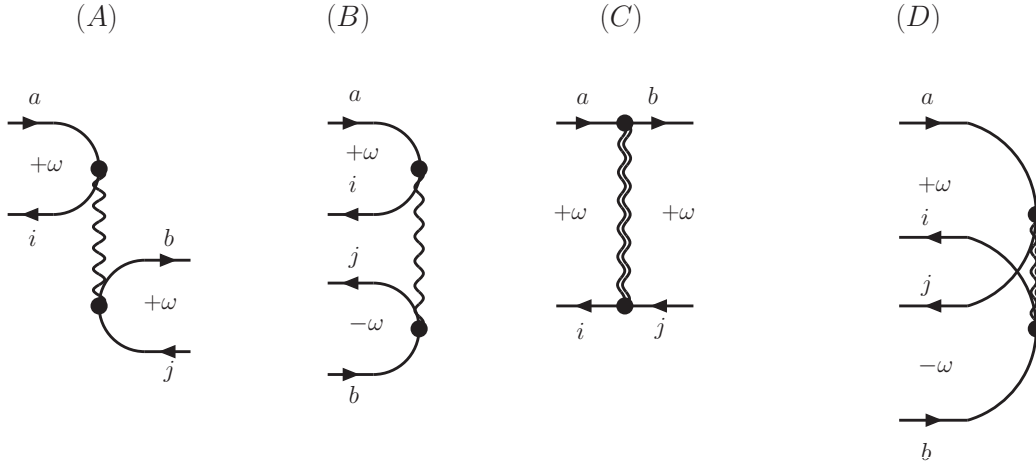


Figure 7.2.: Graphical representation (Goldstone diagrams) for two particle interactions through the Coulomb potential V (wiggly line) and the static screened interaction W (double wiggly line) between electron ($\rightarrow$) and hole ($\leftarrow$), where a/b refers to unoccupied and i/j to occupied states. (A) + (C) corresponds to the resonant-resonant coupling between incoming e/h-pairs (a, i) and outgoing e/h-pairs (b, j) . Picture (A): e/h-pair (a, i) is destroyed at point $\mathbf{r}$ annihilating into a new pair (b, j) at point $\mathbf{r}'$. Picture (C): scattering process of (a, i) into (b, j) . (B)+(D) describe the coupling between resonant and antiresonant e/h-pairs. Picture (B): incoming pair (a, i) with positive frequency annihilates with pair (b, j) associated with negative frequency. Picture (D): e/h-pair (a, i) scatters into pair (b, j) associated to negative frequency.

7.4. Solving the Bethe-Salpeter equation

According to the previous two sections, one needs to solve the Bethe-Salpeter equation for P in the frequency domain given by a Dyson like equation [compare Eq.(7.6)]

$$P(\omega) = P_0(\omega) + P_0(\omega)I P(\omega), \quad (7.21)$$

where I is given by Eq.(7.8). It is natural to discretize the one-particle Hilbert space by restricting it to the span of the N orbitals occupied in the non-interacting reference ground-state (given by a Slater determinant) and a (finite) number of M unoccupied orbitals (corresponding to excitations out of the reference ground-state). This induces a discretization of the fermionic Fock space $\mathcal{F}_+(\mathcal{H})$ over $\mathcal{H}$. Correspondingly, P , V and W turn into finite matrices in the orbital indices. In particular, $P(\omega)$ is now a frequency dependent matrix. Before continuing, we note that the Dyson equation implies that P can be chosen to span the exact same Hilbert space as P_0 , which can be shown easily by iterating the Dyson equation [Eq.(7.21)]. It is hence convenient to restrict the two particle space to a subspace $\mathcal{B}$ of products of M unoccupied orbitals a , and N occupied orbitals i , $\varphi_i \otimes \varphi_a^* \in \mathcal{B}_0$ [first term in Eq.(7.16)] and $\varphi_a \otimes \varphi_i^* \in \mathcal{B}'_0$ [second term in Eq.(7.16)]. The dimension of $\mathcal{B}$ is $2MN$ and the subspace can be decomposed in terms of $\mathcal{B} = \mathcal{B}_0 \oplus \mathcal{B}'_0$ with $\dim \mathcal{B}_0 = \dim \mathcal{B}'_0 = MN$. With this choice $P(\omega)$ can be simply calculated

according to

$$P(\omega) = [P_0(\omega)^{-1} - I]^{-1}. \quad (7.22)$$

Introducing the resonant Φ_K^r and antiresonant Φ_K^a two-orbital states (spanning $\mathcal{B}_0$ and $\mathcal{B}'_0$ respectively),

$$\begin{aligned} \Phi_K^r(\mathbf{r}, \mathbf{r}') &:= \varphi_i(\mathbf{r}) \varphi_a^*(\mathbf{r}') \\ \Phi_K^a(\mathbf{r}, \mathbf{r}') &:= \varphi_a(\mathbf{r}) \varphi_i^*(\mathbf{r}') \end{aligned} \quad (7.23)$$

with the super-index $K = (i, a)$ ($i \in \text{occ.}, a \in \text{unocc.}$), the static interaction kernel I [c.f. Eq.(7.8)] reduces to coupling matrix elements, where the resonant-resonant coupling reads

$$\mathcal{H}_{KJ}^{(r,r)} := \int d\mathbf{r}_1 \dots d\mathbf{r}_4 \Phi_K^r(\mathbf{r}_2, \mathbf{r}_4) I(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \Phi_J^r(\mathbf{r}_3, \mathbf{r}_1).$$

The other interactions are defined analogously. With the restriction of Eq.(7.8) and the definition of Eq.(7.19) and Eq.(7.20), we can write all coupling terms in the following compact manner:

$$\mathcal{H}_{KJ}^{(r,r)} = \langle bi|V|ja\rangle - \langle bi|W|aj\rangle = V_{bi}^{ja} + W_{bi}^{aj} \quad (7.24)$$

$$\mathcal{H}_{KJ}^{(a,a)} = \langle ja|V|bi\rangle - \langle ja|W|ib\rangle = V_{ja}^{bi} + W_{ja}^{ib} \quad (7.25)$$

$$\mathcal{H}_{KJ}^{(r,a)} = \langle ji|V|ba\rangle - \langle ji|W|ab\rangle = V_{ji}^{ba} + W_{ji}^{ab} \quad (7.26)$$

$$\mathcal{H}_{KJ}^{(a,r)} = \langle ba|V|ji\rangle - \langle ba|W|ij\rangle = V_{ba}^{ji} + W_{ba}^{ij}, \quad (7.27)$$

with the second super index $J = (j, b)$ ($j \in \text{occ.}, b \in \text{unocc.}$). Using a graphical representation and considering the explicit time ordering, as commonly adopted for Goldstone diagrams, the first term in Eq.(7.24) describes an annihilation process [Fig. 7.2(A)] with the subsequent creation of a new e/h pair, whereas the second term involves the scattering process between an electron and a hole [Fig. 7.2(C)]. The same processes appear also in Eq.(7.25) and result from the complex conjugated pair. The third coupling term [Eq.(7.26)] involves matrix elements of the interaction I between resonant and antiresonant two-orbital states. Here, the first term corresponds to an annihilation of an e/h-pair against a conjugated h/e-pair [Fig. 7.2(B)], and the second term describes the exchange process where the electron in the first pair annihilates against the hole in the second pair (and vice versa) [Fig. 7.2(D)]. The final equation describes the same process for the conjugated pairs. The inverse of $P(\omega)$ is rewritten in a matrix form

$$\underbrace{\begin{pmatrix} \omega \mathbb{1} & 0 \\ 0 & -\omega \mathbb{1} \end{pmatrix}}_{\omega \Delta} + \begin{pmatrix} P_0^{-1}(0) & 0 \\ 0 & P_0^{-1}(0) \end{pmatrix} - \begin{pmatrix} \mathcal{H}^{(r,r)} & \mathcal{H}^{(r,a)} \\ \mathcal{H}^{(r,a)*} & \mathcal{H}^{(a,a)} \end{pmatrix}, \quad (7.28)$$

where $P_0(0)$ is the frequency independent part of the previously defined time-reduced free 4-point propagator involving only energy differences:

$$(P_0^{-1})_J^K(0) = -(\varepsilon_a - \varepsilon_i) \delta_b^a \delta_j^i. \quad (7.29)$$

It is common to define the matrices A and B as

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} = \begin{pmatrix} \mathcal{H}^{(r,r)} & \mathcal{H}^{(r,a)} \\ \mathcal{H}^{(r,a)*} & \mathcal{H}^{(r,r)*} \end{pmatrix} - \begin{pmatrix} P_0^{-1}(0) & 0 \\ 0 & P_0^{-1}(0) \end{pmatrix}. \quad (7.30)$$

To determine $P(\omega)$ in Eq.(7.22), one needs to determine the poles of $P_0(\omega)^{-1} - I$, i.e. those frequencies Ω where the determinant of Eq.(7.28) is zero valued [164]. Hence one has to solve the resultant generalized eigenvalue problem (EVP)

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \Omega \Delta \begin{pmatrix} X \\ Y \end{pmatrix}. \quad (7.31)$$

For real-valued orbitals in the one-particle Hilbert space, the matrices A and B are real valued and the expression can be fairly easily recast into a symmetric eigenvalue problem. [158, 159] This is, however, not possible in the present case, since B and A are complex, albeit Hermitian matrices.

As we work in a Bloch basis, we can instead proceed along the following lines. If we are interested in the response function at the wave vector $\mathbf{q} = 0$, only pairs of states $K = (i, a)$ at the same wave vectors in the Brillouin zone need to be considered, $K = (i\mathbf{k}, a\mathbf{k})$. The super index now consists of two orbital indices i and a and an additional index for the wave vector $\mathbf{k}$.

Time-inversion symmetry implies that for a Bloch eigenstate $\varphi_{n\mathbf{k}}$ of a one-particle Hamiltonian with eigenvalue $\varepsilon_n(\mathbf{k})$, the orbital $\varphi_{n,-\mathbf{k}}(\mathbf{r}) = \varphi_{n\mathbf{k}}^*(\mathbf{r})$ is also an eigenfunction with the same eigenvalue. We use this property to replace orbitals at $\mathbf{k}$ by those at $-\mathbf{k}$ in the antiresonant two-particle basis. As a first simple example, we consider the independent particle case P_0 [Eq.(7.16)]:

$$\sum_{\substack{\mathbf{k} \\ a \in \text{unocc} \\ i \in \text{occ}}} w_{\mathbf{k}} \frac{\varphi_{a\mathbf{k}}(\mathbf{r}_1) \varphi_{i\mathbf{k}}^*(\mathbf{r}_3) \varphi_{i\mathbf{k}}(\mathbf{r}_2) \varphi_{a\mathbf{k}}^*(\mathbf{r}_4)}{\omega - (\varepsilon_{a\mathbf{k}} - \varepsilon_{i\mathbf{k}}) + \beta\eta} + \sum_{\substack{\mathbf{k}' \\ a \in \text{unocc} \\ i \in \text{occ}}} w_{\mathbf{k}'} \frac{\varphi_{i\mathbf{k}'}(\mathbf{r}_1) \varphi_{a\mathbf{k}'}^*(\mathbf{r}_3) \varphi_{a\mathbf{k}'}(\mathbf{r}_2) \varphi_{i\mathbf{k}'}^*(\mathbf{r}_4)}{-\omega - (\varepsilon_{a\mathbf{k}'} - \varepsilon_{i\mathbf{k}'}) + \beta\eta}, \quad (7.32)$$

where $w_{\mathbf{k}}$ are $\mathbf{k}$ -point weights summing to 1. By replacing $\varphi_{n,\mathbf{k}'}(\mathbf{r}) = \varphi_{n,-\mathbf{k}'}^*(\mathbf{r}) = \varphi_{n\mathbf{k}}^*(\mathbf{r})$, one immediately obtains for the antiresonant part

$$\sum_{\substack{\mathbf{k} \\ a \in \text{unocc} \\ i \in \text{occ}}} w_{\mathbf{k}} \frac{\varphi_{i\mathbf{k}}^*(\mathbf{r}_1) \varphi_{a\mathbf{k}}(\mathbf{r}_3) \varphi_{a\mathbf{k}}^*(\mathbf{r}_2) \varphi_{i\mathbf{k}}(\mathbf{r}_4)}{-\omega - (\varepsilon_{a\mathbf{k}} - \varepsilon_{i\mathbf{k}}) + \beta\eta},$$

which is the resonant term with the position coordinates exchanged. A convenient choice, for the resonant basis and the antiresonant basis is therefore given by:

$$\begin{aligned} \Phi_K^r(\mathbf{r}, \mathbf{r}') &:= \varphi_{i\mathbf{k}}(\mathbf{r}) \varphi_{a\mathbf{k}}^*(\mathbf{r}') \\ \Phi_K^a(\mathbf{r}, \mathbf{r}') &:= \varphi_{a\mathbf{k}}^*(\mathbf{r}) \varphi_{i\mathbf{k}}(\mathbf{r}') \end{aligned} \quad (7.33)$$

It is then easy to show that in this basis, $\mathcal{H}$ is of the form

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix}, \quad (7.34)$$

where A and B are still Hermitian matrices. For instance, the Hartree term in the antiresonant-antiresonant block becomes (commas are introduced to separate the two bra and two ket states)

$$\begin{aligned} \mathcal{H}_{KJ}^{(a,a)} &= \langle j-\mathbf{k}, a-\mathbf{k}' | v | b-\mathbf{k}, i-\mathbf{k}' \rangle \\ &= \langle b\mathbf{k}, i\mathbf{k}' | v | j\mathbf{k}, a\mathbf{k}' \rangle = \mathcal{H}_{KJ}^{(r,r)}. \end{aligned}$$

Similar relations apply to the exchange term involving W , as well as the coupling terms between resonant and antiresonant contributions. For the Hartree term, even the antiresonant-resonant block becomes identical to the resonant-resonant block

$$\langle j-\mathbf{k}, i\mathbf{k}' | v | b-\mathbf{k}, a\mathbf{k}' \rangle = \mathcal{H}_{KJ}^{(r,r)},$$

i.e. as in TDA, a single calculation suffices to set up all terms involving the bare Coulomb operator V , and the A and B matrices only differ by the diagonal matrix $A = B + P_0(0)^{-1}$. For the RPA and TDDFT case, setup of the matrices is therefore not more expensive than for TDA calculations. Only for the exchange term involving W additional matrix elements corresponding to Fig. 7.2(D) need to be calculated.

The solution to the generalized eigenvalue problem [Eq.(7.31)] can be performed by a method discussed e.g. by Stratman et al. [158] and in great detail by Furche.[165, 159] We summarize some aspects briefly.

Introducing a partition of the eigenvector Λ in $\mathcal{B}$ as

$$\begin{pmatrix} X_\Lambda \\ Y_\Lambda \end{pmatrix}, \quad (7.35)$$

where $X_\Lambda \in \mathcal{B}_0$ and $Y_\Lambda \in \mathcal{B}'_0$, the generalized EVP reads

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix} \begin{pmatrix} X_\Lambda \\ Y_\Lambda \end{pmatrix} = \Omega_\Lambda \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \begin{pmatrix} X_\Lambda \\ Y_\Lambda \end{pmatrix}. \quad (7.36)$$

This is equivalent to the system of equations

$$\begin{aligned} AX_\Lambda + BY_\Lambda &= \Omega_\Lambda X_\Lambda \\ -BX_\Lambda - AY_\Lambda &= \Omega_\Lambda Y_\Lambda \end{aligned} \quad (7.37)$$

or

$$(A - B)(X_\Lambda - Y_\Lambda) = \Omega_\Lambda(X_\Lambda + Y_\Lambda) \quad (7.38)$$

$$(A + B)(X_\Lambda + Y_\Lambda) = \Omega_\Lambda(X_\Lambda - Y_\Lambda). \quad (7.39)$$

From Eq.(7.38) and Eq.(7.39) one obtains the relation

$$(A - B)(A + B)\mathbb{1}(X_\Lambda + Y_\Lambda) = \Omega_\Lambda^2 (X_\Lambda + Y_\Lambda). \quad (7.40)$$

The advantage of Eq.(7.40) is that it is formulated in $\mathcal{B}_0$ exclusively, however, it still does not correspond to a Hermitian eigenvalue problem. This can be cured by introducing the identify $\mathbb{1} = (A - B)^{\frac{1}{2}}(A - B)^{-\frac{1}{2}}$ in Eq.(7.40) and defining

$$S = (A - B)^{\frac{1}{2}}(A + B)(A - B)^{\frac{1}{2}} \quad (7.41)$$

$$z_\Lambda = (A - B)^{-\frac{1}{2}}(X_\Lambda + Y_\Lambda) \quad (7.42)$$

such that

$$S z_\Lambda = \Omega_\Lambda^2 z_\Lambda. \quad (7.43)$$

Note that all eigenvalues come in pairs with positive and negative frequencies $\pm\Omega_\Lambda$ corresponding to the resonant and antiresonant part of the response function. On the other hand, from Eq.(7.38) and Eq.(7.42) it follows

$$(X_\Lambda - Y_\Lambda) = (A - B)^{-\frac{1}{2}} \Omega_\Lambda z_\Lambda. \quad (7.44)$$

This equation and Eq.(7.42) allow to determine X_Λ and Y_Λ . However, the "super"-vector (X_Λ, Y_Λ) is not necessarily normalized [i.e. $(X_\Lambda, Y_\Lambda)\Delta(X_\Lambda, Y_\Lambda)^* \neq 1$]. Since the eigenvectors of equation (7.43) are only defined but for a scaling constant. Correct normalization can be achieved by multiplying each eigenvector z_Λ of the squared problem with a suitable scaling factor $z_\Lambda \rightarrow |\Omega_\Lambda|^{-\frac{1}{2}} z_\Lambda$ before solving the two linear equations [Eqs.(7.42), (7.44)]:

$$(X_\Lambda + Y_\Lambda) = \underbrace{(A - B)^{\frac{1}{2}} |\Omega_\Lambda|^{-\frac{1}{2}}}_{C} z_\Lambda \quad (7.45)$$

$$(X_\Lambda - Y_\Lambda) = \pm \underbrace{(A - B)^{-\frac{1}{2}} |\Omega_\Lambda|^{\frac{1}{2}}}_{C'} z_\Lambda, \quad (7.46)$$

where the plus sign applies to positive eigenvalues $+\Omega_\Lambda$, and the minus sign to the negative eigenvalues $-\Omega_\Lambda$. It is then simple to prove that[165]

$$(X_\Lambda + Y_\Lambda) \cdot (X_\Lambda - Y_\Lambda)^* = 1 \quad (7.47)$$

$$X_\Lambda Y_\Lambda^* - Y_\Lambda X_\Lambda^* = 0 \quad (7.48)$$

and eventually $(X_\Lambda, Y_\Lambda)\Delta(X_\Lambda, Y_\Lambda)^* = 1$, if the vectors z_Λ form an orthonormal set. The solution of the squared EVP [Eq.(7.43)] yields two frequencies $\pm\Omega_\Lambda$ and the two corresponding eigenvectors $(X_\Lambda^\pm, Y_\Lambda^\pm)$ read

$$\begin{pmatrix} X_\Lambda^\pm \\ Y_\Lambda^\pm \end{pmatrix} = \frac{1}{2} \begin{pmatrix} (C \pm C')z_\Lambda \\ (C \mp C')z_\Lambda \end{pmatrix}. \quad (7.49)$$

We note, however, that in most cases, it suffices to calculate $X_\Lambda^+ + Y_\Lambda^+$ as shown below for the

polarizability. This sum of the eigenvectors can be trivially obtained from Eq.(7.45).

A few points need to be emphasized here. (i) The matrices A and B are both Hermitian. (ii) To determine $(A - B)^{1/2}$ [Eq.(7.43)], $(A - B)$ needs to be positive definite to make its square roots well defined and single-valued. Since A and B are Hermitian, so is $(A - B)$. Furthermore the eigenvalues of $(A - B)$ are not only real but also positive, because positive definiteness of $(A \pm B)$ guarantees the stability of the reference state $|\Psi_0\rangle$ from which excitations are considered.[166, 167, 165] For TDDFT, if $|\Psi_0\rangle$ is the (stable) groundstate, $(A \pm B)$ is positive definite and thus the excitation energies Ω_Λ are positive. Of course for GW+BSE, the positive definiteness is not guaranteed as the groundstate is not determined fully consistently with the subsequent BSE calculations. However, in all cases considered here the solutions were well defined and eigenvalues of $(A-B)$ are checked to be positiv.

A final comment on the RPA and TDDFT case is in place here. As emphasized before, for RPA and TDDFT the difference matrix $(A - B)$ is a simple diagonal matrix with the eigenvalue differences between the conduction and valence band energies in the diagonal [compare Eq.(7.29)]. This shows that the matrix is always positive definite, and the calculation of $(A - B)^{1/2}$ can be done at essentially no extra cost. Hence, RPA and TDDFT calculations using Casida's equation beyond TDA can be done at *no extra cost compared to TDA*.

The macroscopic dielectric function (DF) ϵ_M is finally obtained from the polarizability P : [62]

$$\epsilon_M(\mathbf{q}, \omega) = 1 - \lim_{\mathbf{q} \rightarrow 0} \left[v(\mathbf{q}) \int d\mathbf{r}_1 d\mathbf{r}_2 e^{-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} P(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_2, \omega) \right]. \quad (7.50)$$

By exploiting the orbital representation [Eq.(7.17)] and the spectral representation [c.f. (A18) in Ref. [165]] of $P(\omega)$, the DF [62] reads in terms of the eigenvectors $(X_\Lambda^+, Y_\Lambda^+)$

$$\begin{aligned} \epsilon_M(\mathbf{q}, \omega) = 1 + \lim_{\mathbf{q} \rightarrow 0} v(\mathbf{q}) \sum_{\Lambda} \left(\frac{1}{\Omega_\Lambda - \omega} + \frac{1}{\Omega_\Lambda + \omega} \right) \times \\ \left\{ \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{a,i} \langle a\mathbf{k} | e^{i\mathbf{q}\cdot\mathbf{r}} | i\mathbf{k} \rangle X_\Lambda^{+(i,a)\mathbf{k}} + \right. \\ \left. \langle i - \mathbf{k} | e^{i\mathbf{q}\cdot\mathbf{r}} | a - \mathbf{k} \rangle Y_\Lambda^{+(a,i)-\mathbf{k}} \right\} \times \left\{ c.c. \right\}. \end{aligned} \quad (7.51)$$

Using time inversion symmetry, the transition probabilities (term in curly brackets) simplify to

$$\sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{a,i} \langle a\mathbf{k} | e^{i\mathbf{q}\cdot\mathbf{r}} | i\mathbf{k} \rangle \left[X_\Lambda^{+(i,a)\mathbf{k}} + Y_\Lambda^{+(a,i)-\mathbf{k}} \right]. \quad (7.52)$$

Equation (7.51) assumes that the $\mathbf{q} = 0$ component of Coulomb kernel v has been set to zero, when evaluating the matrix elements of V in Eq.(7.24-7.27), as discussed in detail in Ref. [62]. One can derive this result by observing that the relation between the reducible (two point)

polarizability χ and independent particle polarizability χ_0 is given by

$$\chi^{-1} = \underbrace{\chi_0^{-1}}_{\bar{\chi}^{-1}} - \bar{v} - v_0. \quad (7.53)$$

Here v_0 is the (usually diverging) Coulomb kernel at the wave vector $\mathbf{q} = 0$, and $\bar{v}$ is the rest. The standard equation for the macroscopic dielectric constant is

$$\epsilon_M^{-1} = (1 + v\chi)_{00} \quad (7.54)$$

$$= (1 + v_0(\bar{\chi}^{-1} - v_0)^{-1})_{00} \quad (7.55)$$

where, the subindex 00 implies evaluation of the matrix elements at $\mathbf{q} = 0$. Straightforward algebraic manipulation of the term after the second equation sign yields

$$\epsilon_M = 1 - v_0\bar{\chi}, \quad (7.56)$$

which corresponds to Eq.(7.51). This equation is most likely used in most solid state BSE codes to evaluate the dielectric constant. It is important to note that the summation is over positive and negative frequency branches, thus restoring the sum of the resonant and antiresonant part, even in the TDA case. Strictly speaking such an implementation goes beyond what the TDA does (entirely neglecting one frequency branch).

7.5. Dielectric function at finite $\mathbf{q}$ -vectors

For finite momentum transfer $\mathbf{q}$, the two orbital basis reads

$$\begin{aligned} \Phi_{K\mathbf{q}}^r(\mathbf{r}, \mathbf{r}') &:= \varphi_{i,\mathbf{k}}(\mathbf{r})\varphi_{a,\mathbf{k}+\mathbf{q}}^*(\mathbf{r}') \\ \Phi_{K\mathbf{q}}^a(\mathbf{r}, \mathbf{r}') &:= \varphi_{a,\mathbf{k}'}(\mathbf{r})\varphi_{i,\mathbf{k}'+\mathbf{q}}^*(\mathbf{r}') = \varphi_{a,\mathbf{k}+\mathbf{q}}^*(\mathbf{r})\varphi_{i,\mathbf{k}}(\mathbf{r}'), \end{aligned} \quad (7.57)$$

where we have used time-inversion symmetry in the second line. With the definition Eq.(7.57), matrix elements of $\mathcal{H}$ are set up in a similar manner as in Eqs.(7.24-7.27). For the sake of clarity, we will show the relation for the antiresonant-antiresonant coupling pair for the Hartree-kernel V . At finite momentum transfer, the resonant-resonant matrix element reads

$$\mathcal{H}_{K\mathbf{q}J\mathbf{q}}^{(r,r)} = \langle b\mathbf{k} + \mathbf{q}, i\mathbf{k}' | v_{\mathbf{q}} | j\mathbf{k}, a\mathbf{k}' + \mathbf{q} \rangle. \quad (7.58)$$

Replacing the momenta in the antiresonant two-orbital state $\Phi_{K\mathbf{q}}^a$ by $\mathbf{k} \rightarrow -\mathbf{k}$ and $\mathbf{k}+\mathbf{q} \rightarrow -\mathbf{k} - \mathbf{q}$ we find

$$\begin{aligned} \mathcal{H}_{K\mathbf{q}J\mathbf{q}}^{(a,a)} &= \langle j - \mathbf{k} - \mathbf{q}, a - \mathbf{k}' | v_{-\mathbf{q}} | b - \mathbf{k}, i - \mathbf{k}' - \mathbf{q} \rangle \\ &= \langle b\mathbf{k}, i\mathbf{k}' + \mathbf{q} | v_{-\mathbf{q}} | j\mathbf{k} + \mathbf{q}, a\mathbf{k}' \rangle \\ &= \langle b\mathbf{k} + \mathbf{q}, i\mathbf{k}' | v_{\mathbf{q}} | j\mathbf{k}, a\mathbf{k}' + \mathbf{q} \rangle \\ &= \mathcal{H}_{K\mathbf{q}J\mathbf{q}}^{(r,r)}. \end{aligned}$$

The same relation also holds for matrix elements involving W and the entire matrix $\mathcal{H}$ has the same algebraic structure as in the case of vanishing $\mathbf{q}$ vectors [Eq.(7.34)]. The dielectric function is finally evaluated as

$$\epsilon_M^{-1}(\mathbf{q}, \omega) = 1 - v(\mathbf{q}) \sum_{\Lambda} \left(\frac{1}{\Omega_{\Lambda} - \omega} - \frac{1}{\Omega_{\Lambda} + \omega} \right) \times \left\{ \sum_{\mathbf{k}} w_{\mathbf{k}} \sum_{a,i} \langle a\mathbf{k} + \mathbf{q} | e^{i\mathbf{q} \cdot \mathbf{r}} | i\mathbf{k} \rangle \left(X_{\Lambda}^{+(i,a)\mathbf{k}+\mathbf{q}} + Y_{\Lambda}^{+(a,i)-\mathbf{k}-\mathbf{q}} \right) \right\} \times \left\{ c.c. \right\}. \quad (7.59)$$

Note that at finite $\mathbf{q}$, the full Coulomb kernel is used without disregarding any component, we thus rely on the standard expression for the macroscopic dielectric function (7.54). If the $q = 0$ component of Coulomb kernel v had not been set to zero in the previous section, one would have to use Eq.(7.59) as well (compare Eq.(2.7) and (2.9) in [62]). The divergence of the Coulomb kernel is then canceled by the orthogonality relation between occupied and un-occupied states, and k.p perturbation theory must be used to obtain the long wave length contributions to the two-electron four orbital integrals of the Coulomb kernel (for the PAW method see e.g. [168]). Our RPA-GW implementation for instances uses Eqs.(7.54,7.59) to determine the dielectric matrix, whereas the BSE code relies on the simpler to implement relation (7.51). Both yield *exactly identical results* as both relations are algebraically equivalent (compare previous section). Matter of fact, at any momentum transfer $\mathbf{q}$, both codes (GW and BSE) yield exactly identical results for the RPA (the GW code uses two-point polarizabilities and can be applied only to the RPA).

A subtle point however needs to be considered. In the TDA case, Eq.(7.51) and Eq.(7.59) are no longer equivalent, with the first equation yielding significantly more accurate results. Eq.(7.51) disregards the coupling at all wave vectors different from $\mathbf{q} = 0$, but reintroduces the antiresonant contribution exactly in the final evaluation of the macroscopic dielectric constant; furthermore the equation is additive in dielectric constant. Eq.(7.59) is additive in the inverse of the dielectric constant, and if ϵ_M needs to be determined, it is not obvious whether the antiresonant part should be added before or after inversion. In both cases, TDA results differ from Eq.(7.51) as well as from the full treatment. As to why, equation (7.51) is more accurate, we return to the derivation at the end of the previous section. Using (7.56), one first calculates $\bar{\chi}^{-1} = \chi_0^{-1} - \bar{v}$ neglecting the resonant-antiresonant coupling. However, when determining ϵ_M the fully restored $\bar{\chi}$ is used, implying that the resonant-antiresonant coupling at $\mathbf{q} = 0$ is exactly accounted for. Eqs.(7.54,7.59) are fundamentally different, they include the self-consistent response of the electrons to their own field from the outset, as Eq.(7.53) can be rephrased as,

$$\chi = \chi_0 + \chi_0 v \chi_0 + \chi_0 v \chi_0 v \chi_0 + \dots$$

If only the resonant part is included in χ_0 , the selfconsistent response to the incorrect (resonant only) part is included in the evaluation of the polarization propagator. There is no way to restore the correct response including the antiresonant part a posteriori. Thus Eq.(7.51) is preferable to

Table 7.1.: PAW potentials used in the present work. The columns $r_{s,p,d}$ specify the core radii for each angular quantum number in a.u. The “default” plane wave cutoff energy $E_{\text{cut}}^{\text{pw}}$ for the orbitals is specified in eV. Column “local” specifies the chosen local potential. This is usually the all-electron potential replaced by a soft approximation inside the specified core radius.

	r_s	r_p	r_d	local	$E_{\text{cut}}^{\text{pw}}$
C	1.20	1.20	1.50	d	413
Si	1.90	1.90	1.90	d	245
Li	1.40	1.40	1.40	d	498
F	1.20	1.52	1.50	d	400

Eq.(7.59) and goes beyond TDA, since it correctly includes beyond TDA contributions at $\mathbf{q} = 0$. To resolve this issue at finite $\mathbf{q}$, one should clear the Coulomb kernel at the considered wave vector $\mathbf{q}$, and apply Eq.(7.51), an approach we might want to test in future work.

This line of thought also implies that many solid state TDDFT and BSE codes yield results much superior to what the TDA should yield. It also explains why errors in the TDA are often substantial in quantum chemistry codes, which can not easily single out the most relevant wave vector $\mathbf{q} = 0$, and often rely on Eq.(7.59) to determine the response function.

7.6. Computational methods

7.6.1. PAW method and potential parameters

The *ab initio* calculations presented in the paper employ a plane-wave basis set and are performed using the VASP code. [169, 170] The potentials are generated using the projector augmented wave method (PAW) [138] to describe interactions between valence electrons and ionic cores (for details see Table 7.1). We use the PAW implementation of Kresse and Joubert. [142] The computational procedure is the following. For each system we perform a standard DFT calculation to obtain the Kohn-Sham orbitals and Kohn-Sham one-electron energies. The exchange-correlation part is approximated by the functional of Perdew, Burke, and Ernzerhof (PBE) [37] for silicon, whereas the local density approximation (LDA) is employed for lithium fluoride and carbon. The results are, however, independent of the starting point for the materials considered here. The subsequently calculated quasiparticle (QP) energies and orbitals are calculated within a self-consistent (sc) QPGW₀ approach. [72, 73, 74] The QP energies and QP orbitals are updated iteratively. The screened interaction W_0 is kept fixed at the RPA level using the original Kohn-Sham orbitals and one-electron energies. Within the sc-QPGW₀ calculations, a Hermitian eigenvalue problem is solved [c.f. Eq. (3) in Ref. [74]]

$$\bar{S}^{-1/2} \bar{H} \bar{S}^{-1/2} \bar{U} = \bar{U} \bar{\Lambda}. \quad (7.60)$$

Initially, the QP Hamiltonian $\bar{H}$ [c.f. Eq. (2) in Ref. [74]] is expressed in the basis set $\{\phi_n^{(1)}\}$, for which we use DFT orbitals. In iteration i , the solution of Eq.(7.60) yields the diagonal matrix $\bar{\Lambda}$ with the eigenvalues $E_n^{(i+1)}$ and the unitary matrix $\bar{U}$ holds the corresponding eigenvectors of

$\bar{H}(\{E_n^{(i)}\}, \{\phi_n^{(i)}\})$. After that, the QP Hamiltonian $\bar{H}(\{E_n^{(i+1)}\}, \{\phi_n^{(i+1)}\})$ is set up with the new eigenvalues and eigenfunctions $\phi_n^{(i+1)} = \sum_m U_{mn} \phi_m^{(i)}$. The corresponding new eigenvalue problem is solved in the new basis set. This procedure is iterated until self-consistency is reached. We perform seven self-consistency steps, which gives QP energies converged to about 1 meV. After the final step, the optical matrix elements are recalculated using the final sc-QPGW₀ orbitals, and the screened Coulomb kernels W_0 are stored. In the final step, the BSE matrix is set up and the EVP Eq.(7.36) is solved.

7.6.2. Symmetry reduced k-point meshes

To reduce the computational demand, we apply a method that was first introduced in Ref. [171]. A similar approach was later also discussed in Ref. [172].

Table 7.2.: The column $\mathcal{L}$ specifies the number of irreducible $\mathbf{k}$ -points obtained from an ordinary $n \times n \times n$ $\mathbf{k}$ -mesh, Γ -centred or Monkhorst-Pack (shifted off Γ). Calculations are then performed on $\mathcal{L}$ new $\mathbf{k}$ -grids ($\mathcal{M}_{p=1\dots\mathcal{L}}$) obtained by shifting a $m \times m \times m$ $\mathbf{k}$ -grid along each irreducible $\mathbf{k}$ -point $\tilde{\mathbf{k}}_{p=1\dots\mathcal{L}}^n$.

	$\mathbf{k}$ -mesh	n	$\mathcal{L}$	$\mathbf{k}$ -mesh ($\mathcal{M}_p$)	m
Si	Γ	3	4	Γ	16
LiF	Γ	4	8	Γ	6
C	MP	4	10	Γ	8

In order to reach an accurate sampling of the Brillouin zone, we perform independent calculations for many $\mathbf{k}$ -point grids systematically shifted off Γ . The systematic shifts are calculated from a symmetry reduced $n \times n \times n$ $\mathbf{k}$ -mesh. The procedure is the following:

- (i) Generate all irreducible $\mathbf{k}$ -points $\tilde{\mathbf{k}}_{p=1\dots\mathcal{L}}^n$ with weight $w_{p=1\dots\mathcal{L}}$ from a Γ -centred or Monkhorst-Pack[173] $n \times n \times n$ $\mathbf{k}$ -mesh.
- (ii) Generate $\mathcal{L}$, $m \times m \times m$ $\mathbf{k}$ -point grids shifted off Γ by the previously calculated shifts $\tilde{\mathbf{k}}_{p=1\dots\mathcal{L}}^n$; this creates $\mathcal{L}$ sets $\mathcal{M}_{p=1\dots\mathcal{L}}$. Calculations are performed independently for each of these sets. The results of each shifted mesh are then weighted by the previously determined weight w_p and summed up.

It is easy to see, that the set $\cup_p \mathcal{M}_p$ includes all $\mathbf{k}$ -points of a regular $(n \cdot m) \times (n \cdot m) \times (n \cdot m)$ $\mathbf{k}$ -mesh with the proper weights. Using this trick the computational time reduces roughly by factor $(n^3)^2$ in the GW calculations and $(n^3)^3$ in the Bethe-Salpeter calculations, at the expense of truncating the long range part of the Coulomb kernel at roughly m times the unit cell size. Since the exciton is well localized in LiF, m can be small for LiF without causing sizeable errors, whereas larger values m are required for C and Si. The used $\mathbf{k}$ -point sets are summarized in Table 7.2.

The dielectric function of Si, C and LiF shown in Figs. (7.3,7.6,7.7) are averaged over the $\mathcal{L}$

independent calculations. The average is calculated as

$$X = \frac{1}{W} \sum_{p=1}^{\mathcal{L}} w_p X_p \quad \text{and} \quad W = \sum_{p=1}^{\mathcal{L}} w_p, \quad (7.61)$$

where X_p denotes the dielectric function calculated on the $\mathbf{k}$ -mesh $\mathcal{M}_p$ shifted by an irreducible $\mathbf{k}$ -point $\tilde{\mathbf{k}}_p^n$.

7.7. Results at vanishing momentum transfer

Previous *ab-initio* calculations for silicon,[62, 174, 175, 93, 176, 91, 177, 178, 92, 179] carbon[91] and lithium fluoride[180, 181, 178] usually included only the resonant part of the BSE-Hamiltonian. Although it is common consensus that the effects of the coupling between the resonant and anti-resonant part are small,[175, 182, 183, 184, 94] optical spectra explicitly including the coupling term have rarely been published. [94, 185, 186, 187]

7.7.1. Residual basis set errors

The calculation of the frequency dependent dielectric function [Eq.(7.51)] requires the summation over all possible transition pairs between occupied and unoccupied states. By imposing a cut-off for the transition states (compare Table 7.3), high energy excitations are neglected. This yields a residual error for the dielectric function at each frequency point. In order to estimate the total residual error for the dielectric constant (Table 7.4) we first calculate $\text{Re } \epsilon_M(\omega=0)$ on a single non-shifted Γ -centred $m \times m \times m$ $\mathbf{k}$ -mesh including 12 unoccupied bands for Si, C and LiF. This calculation is repeated including now only 7 (Si) or 8 (C, LiF) unoccupied bands, with 4 valence bands taken into account in both cases. The residual error $\hat{\epsilon}$ for the dielectric constant on this $\mathbf{k}$ -mesh is the difference of both calculations, i.e. $\hat{\epsilon} = \text{Re } \epsilon_M(\omega=0; 12 \text{ CB}) - \text{Re } \epsilon_M(\omega=0; 7/8 \text{ CB})$, where CB denotes conduction bands. In Table 7.4 the dielectric constants are given without and with these basis set corrections.

Table 7.3.: Number of occupied and unoccupied (virtual) bands included in the calculation of the optical transition matrix elements.

	occupied	virtual
Si	4	7
LiF	4	8
C	4	8

7.7.2. Silicon

Figure 7.3 shows the real and imaginary part of the dielectric function (DF) of silicon. Electron-hole pairs from the 4 valence bands and the lowest 7 conduction bands were included to compute the dielectric function [c.f. Eq.(7.51)]. The turquoise (solid) curve represents the results of a calculation where the full BSE-Hamiltonian is used. First of all, the present spectrum agrees

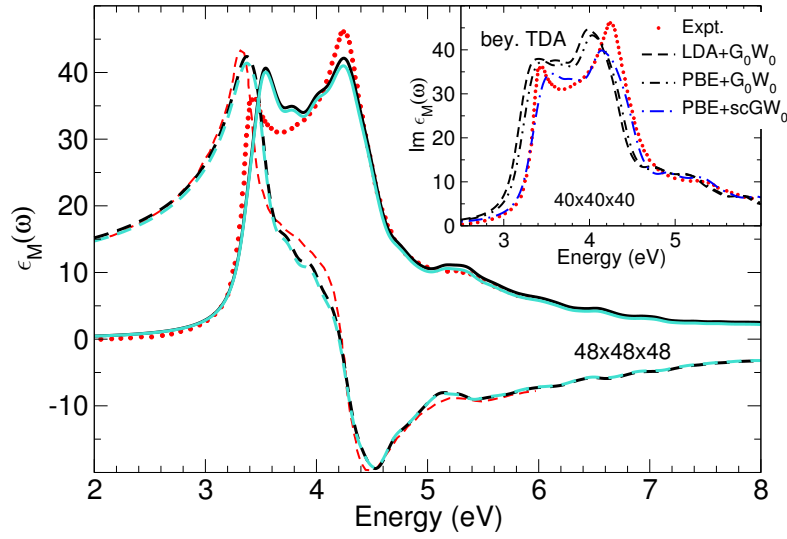


Figure 7.3.: Real and imaginary part of dielectric function ϵ_M ($\Re \epsilon_M / \Im \epsilon_M$) of silicon predicted using sc-QPGW₀+BSE using Tamm-Dancoff approximation (black-dashed/black line) and full BSE (turquoise-dashed/turquoise line) compared to the experimental spectrum (red dots). [188] Theoretical spectra are smoothed by a Lorentzian using a complex shift of 0.1 eV. Inset: comparison of the imaginary part of the dielectric function calculated using (i) LDA (dashed line) and PBE (double-dotted dashed line) orbitals and quasiparticle energies calculated at the G_0W_0 level, and (ii) using self-consistently iterated quasiparticle energies and orbitals (blue dotted-dashed line) based on PBE orbitals and eigenvalues.

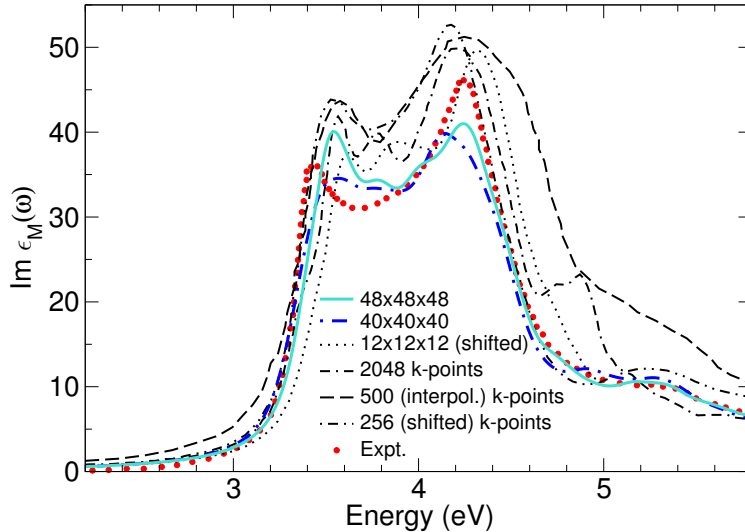


Figure 7.4.: Imaginary part of the dielectric function $\epsilon_M(\omega)$ of silicon for previous calculations compared to our results (turquoise solid and blue dashed-dotted line) with regard to $\mathbf{k}$ -point sampling. In sequence of appearance in figure: (i) Ref. [189] (double-dotted dashed line), Ref. [178] (dashed line), (iii) Ref. [190] (dotted line), (iv) Ref. [175] (double-dashed dotted line). Experimental measurement (red dots). [188]

Table 7.4.: Static dielectric constant $\text{Re } \epsilon_M(\omega=0)$ from the solution of Eq.(7.51) in the Tamm-Dancoff Approximation (TDA) and beyond TDA. The values in parentheses are the corrected dielectric constants, where the estimated residual basis set error is taken into account, i.e. $\text{Re } \epsilon_M(\omega=0) + \hat{\epsilon}$ (see section 7.7.1). Experimental data are taken from Ref. [70].

$\text{Re } \epsilon_M(\omega=0)$	Si	C	LiF
TDA	11.82 (11.87)	5.31 (5.81)	1.76 (1.96)
bey. TDA	11.42 (11.49)	5.25 (5.65)	1.75 (1.89)
Exp.	11.90	5.70	-

very well with the experimental spectrum for the peak positions, although we have not applied any empirical shifts in the preceding quasiparticle calculations to fit the spectrum. Most notably, the position of the pronounced E_1 peak differs only by about 110 meV from experiment (at room temperature [188]) and by about 80 meV compared to measurements at 20K. [191] The E_2 peak position agrees perfectly with the measured spectrum. According to Ref. [192, 191] interband transitions exhibit a temperature dependence with respect to energy shifts and broadening.[193] In particular the E_1 peak position is renormalized due to electron-phonon interactions. Even at zero temperature, zero-point vibrations are suggested to give rise to a shift of about 100 meV [192]. The effect of lattice vibrations has also been calculated entirely *ab-initio* [179] indicating a redshift of about 80 meV for the E_1 and E_2 peaks at $T = 0$ K. This compares favorably to our calculated spectrum which does not include any phonon contributions. The agreement for the intensities is not entirely satisfactory. In particular the E_1 peak is slightly overestimated and the ratio of intensities (E_2/E_1) is nearly one. The present calculations correspond to an exceedingly accurate $\mathbf{k}$ -point sampling of $48 \times 48 \times 48$ points and seem to be reasonably converged with respect to the number of $\mathbf{k}$ -points. However, the interaction range of the exciton is still limited by the $16 \times 16 \times 16$ subset that we used in each individual GW and BSE calculation. In fact, the spectrum is rather sensitive to the selected $\mathbf{k}$ -points as shown in Fig. 7.4. For instance, if the sampling is reduced from $48 \times 48 \times 48$ to $40 \times 40 \times 40$ (and $10 \times 10 \times 10$ for the exciton interaction range) the E_1 and E_2 peaks are less pronounced. This underlines the fact that the exciton in silicon has a rather large spatial extent in real space and a dense $\mathbf{k}$ -point sampling is necessary. To determine how much the starting point influences the results, the inset of Fig. 7.3 shows a comparison of BSE calculations based on G_0W_0 calculations using either PBE or LDA orbitals. The shape of the curves agrees almost perfectly with the sc-QPGW₀+BSE calculations, however, sc-QPGW₀+BSE slightly decreases the amplitudes and shifts the spectrum to the right, thereby improving the agreement with experiment. In Fig 7.4, we compare our results with previous calculations. We suspect that the main reason for discrepancies to previous calculations are the different $\mathbf{k}$ -point sets. None of the previous calculations seems to be very well converged with respect to the number of $\mathbf{k}$ -points. Some $\mathbf{k}$ -point sets, enhance certain features such as the E_1 or E_2 peak. Overall it is obvious that the present calculations match the experimental results much better than previous data.

7.7.3. Dielectric function of silicon at a finite $\mathbf{q}$ -vector

The dielectric function at finite momentum transfer has previously been calculated mainly to investigate the dynamic structure factor [194, 195, 196] or electron energy loss spectra [146]. However, the explicit $\mathbf{q}$ -dependence of the dielectric function has been little explored [183, 184], and results from the solution of the full excitonic Hamiltonian have not been published to the best of our knowledge.

In Fig. 7.5 we show the dielectric function of silicon at a finite wave vector $|\mathbf{q}| = 0.795$ a.u. along the [111] direction at different levels of approximations of the polarizability. The calculations are based on the same $\mathbf{k}$ -point grid as above, but since differences between different shifts are tiny, we have calculated the dielectric function only for a single set of shifted $16 \times 16 \times 16$ $\mathbf{k}$ -points. The highest considered excitation energy was 24 eV, resulting in a BSE-Hamiltonian of roughly 200.000×200.000 if the Tamm-Dancoff approximation is not applied. Results for time dependent DFT were previously published by Weissker *et al.* [183]. The important point of that study was that (i) the independent particle (IP) approximation yields very unsatisfactory results independent of whether the results are based on DFT or GW one electron energies (not shown). (ii) Time dependent DFT yields excellent agreement with experiment. On the level of the RPA, our present data are similar to the previous results, although our present calculations yield less intensity for the peak at 19 eV. The GW+BSE data follow the TDDFT and thus experiments well, although the amplitude is reduced compared to the TDDFT data. For the TDA, the peak around 17 eV clearly disappears, an effect that was also observed for TDDFT in Ref.[183] (Fig. 4). Note that in our TDA calculations we have entirely neglected the antiresonant part i.e. disregarding the negative frequency branch in Eq.(7.59). Including it yields even worse agreement with the beyond TDA spectrum. We can therefore conclude that GW+BSE describes excitonic features at zero wavelength and finite wave length almost equally well, whereas TDDFT works well at finite momentum transfer but fails at zero wave length, as it is not able to resolve the E_1 peak in Si.

7.7.4. Carbon

The optical spectrum of carbon is shown in Figure 7.6(b). Transition energies are considered up to 36 eV including up to 4 valence and 8 conduction bands. As before, the various characteristic positions are reproduced remarkably well, for instance the onset of absorption around 7 eV, the main peak around 12.2 eV, or the "kink" around 13 eV. However, for carbon, the peak intensity in the BSE calculations is significantly overestimated compared to the experimental values. A similar, albeit not as pronounced overestimation, was observed in a previous BSE calculation. [146] This overestimation is most likely caused by exclusion of any temperature effects on the spectrum; as shown in Ref. [179] (only for silicon), there is a gradual redshift of the peak position as well as an increase of the peak width as the temperature increases. As for Si, the difference between TDA and the full BSE equation is almost entirely negligible. The intensity of the main peak differs only by about 2%, so as for Si, it is save to neglect effects beyond the TDA.

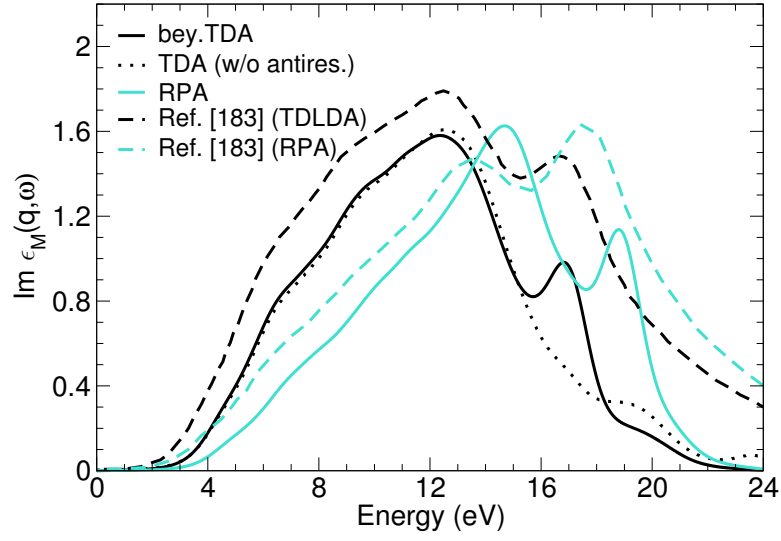


Figure 7.5.: Imaginary part of the dielectric function $\epsilon_M(\mathbf{q}, \omega)$ for silicon at $|\mathbf{q}| = 0.795$ a.u. along the $[111]$ direction at the level of (i) beyond TDA (black solid line), (ii) TDA (without the negative frequency branch in Eq.(7.59)) (dotted line), (iii) RPA (turquoise solid line). Reference spectra for TDLDA (black-dashed line) and RPA (turquoise-dashed line) are taken from Ref. [183].

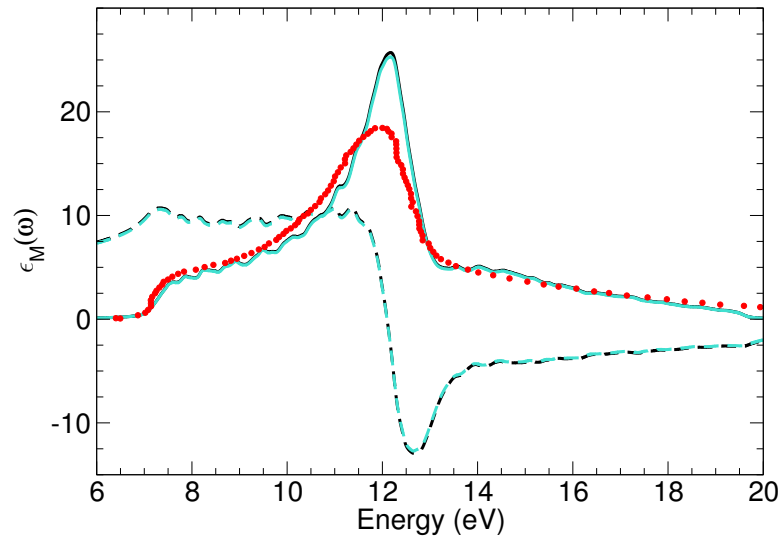


Figure 7.6.: Dielectric function $\epsilon_M(\omega)$ of carbon. Color coding as in Fig. 7.3. Experimental spectrum (red dots). [197]

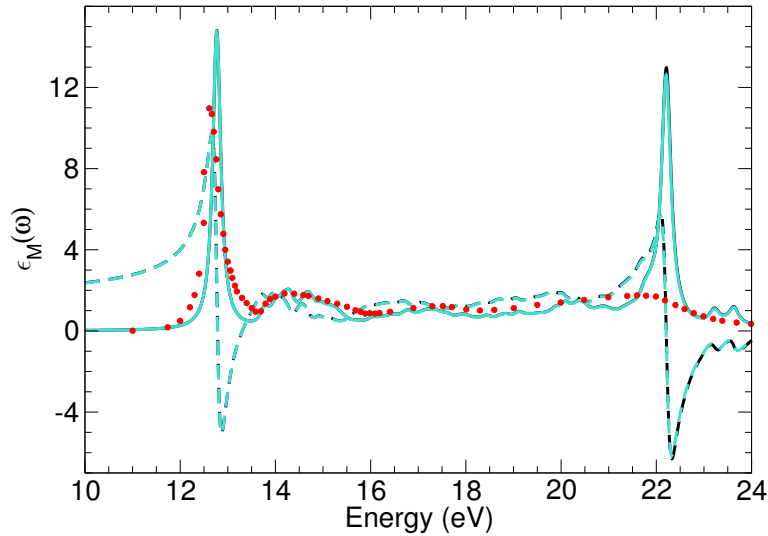


Figure 7.7.: Dielectric function $\epsilon_M(\omega)$ of lithium fluoride. Color coding as in Fig. 7.3. Experimental spectrum (red dots). [198]

7.7.5. Lithium fluoride

The optical spectrum of LiF (Fig. 7.7) is obtained including the highest 4 valence bands and the lowest 8 conduction bands. Comparison to experiment suggest again that the $sc\text{-QPGW}_0\text{+BSE}$ yields excellent results. The first peak is slightly blue shifted compared to the experiment (about 16 meV). At first sight, the first minimum — in the experiment located around 13.6 eV — seems to be red shifted in the calculations. However this could well be a result of the finite experimental resolution or finite temperature broadening of the measured spectrum. As in most previous calculations we also observe an additional sharp peak around 22.2 eV, which is absent in experiment. This peak was also present in all previous BSE calculations[180, 146] and might be an artifact of either the static W kernel or the simplified QP picture used as starting point for the BSE calculations.

In comparison to Si and C, LiF shows almost no differences for the DF calculated within the TDA or solving the full BSE. This is in line with simple perturbation theory, which suggests that the coupling strength between the resonant and antiresonant part will be inverse proportional to the energy difference between the most prominent peaks in the resonant and antiresonant part. Therefore, as the excitation energies increase, beyond TDA effects become less important, which is entirely in line with our observations.

7.7.6. Benchmarking the BSE code - lithium fluoride (dimer)

The previous results for the bulk systems show that solving the full excitonic BSE-Hamiltonian makes only little (Si, C) or almost no contribution (LiF) to the DF compared to the TDA at $\mathbf{q} = 0$. However, for low dimensional systems like molecules, exclusion of the coupling terms of resonant/antiresonant e-h pairs leads to larger errors in the optical spectrum. [94] We choose the cyclic lithium fluoride dimer (Li_2F_2) to demonstrate that the TDA is less satisfactory in

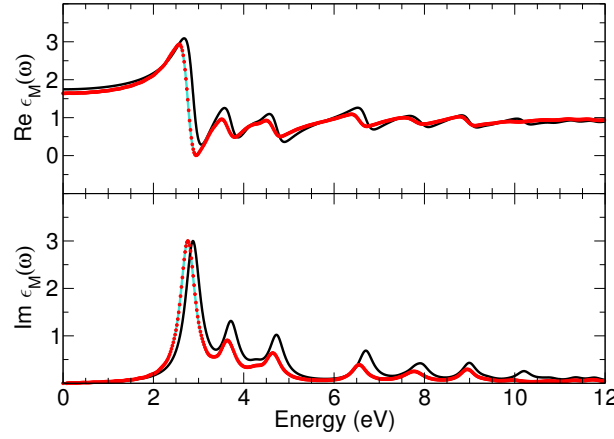


Figure 7.8.: Frequency dependent dielectric function $[\text{Re } \epsilon(\omega)/\text{Im } \epsilon(\omega)]$ for Li_2F_2 obtained from a HF+TD-HF calculation, applying the TDA (black lines) and beyond TDA (turquoise lines). The latter ones are compared to the dielectric function obtained from a real-time propagation of the orbitals on a Hartree-Fock level (red dots). Transition pairs with an energy difference up to 16 eV are included. Structural data are taken from Ref. [199].

describing the dielectric function of low dimensional systems. Moreover, to give evidence that our BSE code works correctly, we compare our results obtained from time-dependent Hartree-Fock (TD-HF) calculations [on top of Hartree-Fock (HF)] against the results from a real-time propagation of the orbitals. Solving the polarizability within the TD-HF approximation requires to solve an eigenvalue problem that is algebraically equivalent to the solution of the excitonic BSE-Hamiltonian. In the framework of TDDFT, this is known as the Casida equation.[155] Computationally, one has to calculate the same matrix elements as given in Eqs.(7.24-7.27). However, the screened Coulomb potential W is replaced by the bare Coulomb exchange kernel. This allows us to use the same routines to calculate the polarizability as in the case of the excitonic BSE-Hamiltonian. On the other hand, propagating orbitals in real time for the HF-Hamiltonian, allows one to calculate the polarizability for TD-HF beyond TDA without any further approximations.[200, 201, 202] We have implemented this time-propagation method in the VASP code and use it to evaluate our results for the DF beyond TDA (obtained from matrix diagonalization). The cyclic dimer Li_2F_2 shows a distinct difference between the dielectric function calculated within the TDA and beyond TDA (Fig. 7.8). Compared to the TDA, the entire spectrum is slightly red-shifted and less pronounced at higher energies, clearly showing that coupling of resonant/antiresonant electron-hole pairs contribute to the polarizability. Similar features in the absorption spectrum have been observed for the *trans*-azobenzene molecule. [94] The overall perfect agreement of the DF using the diagonalization of the TD-HF equation and the time-propagation method confirms the correctness of the exchange terms in the beyond TDA code.

7.8. Summary and conclusion

The purpose of the present paper is two fold. First we have discussed a simple and efficient method to calculate all eigenvalues and eigenvectors of the full BSE and Casida equation for solids (in the absence of spin-orbit coupling). To achieve this goal, we have replaced the orbitals at the $\mathbf{k}$ -points $\mathbf{k}$ by orbitals at the $\mathbf{k}$ -points $-\mathbf{k}$ in the antiresonant part of the BSE matrix. This approach allows to apply methods previously used in the quantum chemistry community: the BSE equation can then be reformulated into a quadratic equation involving the square of the original eigenfrequencies. At the same time, the dimension of the matrix is reduced from $2N$ to N , where N is the number of particle-hole pairs. Instead of a single $2N$ non-Hermitian eigenvalue problem, now two diagonalizations of Hermitian matrices are required. This results in significant savings in compute time. All in all, the present approach is about 2 times more expensive than a standard Tamm-Dancoff calculation, a fairly modest computational increase. Furthermore, for time-dependent DFT, the present approach is as efficient as the Tamm-Dancoff approximation (requiring only few trivial additional calculation steps), and the required modifications of existing codes should be straightforward.

To ascertain the correctness of the implementation, we have compared the present results against a time-evolution code and found that the present approach yields exactly identical results for the Li_2F_2 dimer. Likewise, for the RPA (i.e. neglecting exchange terms), the code yields identical frequency dependent dielectric constants as our GW-RPA implementation at $\mathbf{q} = 0$, as well as at finite momentum transfer $\mathbf{q} \neq 0$. Compared to the time evolution approach, the present method in combination with scaLAPACK is competitive for matrix sizes of up to 100.000-150.000. Most important, it allows to calculate all eigenvectors and eigenvalues, which is difficult for time-evolution and Lanczos algorithms that often only yield the "optical" density of states.

In the present studies, we find that the difference between TDA and beyond TDA results is tiny in most considered simple solids. This observation is in agreement with literature, where many authors have claimed that they have not observed any difference between TDA and beyond TDA (albeit almost always without showing the actual results). A visible change of the dielectric function is only observed for Si at finite wave vectors and for the cyclic dimer Li_2F_2 . In section 7.5 we have argued why the effects beyond TDA are so small. Our implementation, as well as all BSE implementations following Onida et al. [62] include beyond TDA effects (we are not certain, though, whether all BSE codes follow this recipe). They do so by first disregarding the resonant-antiresonant coupling but at the same time disregarding the response at $\mathbf{q} = 0$. However, in the final calculation step determining the macroscopic dielectric constants, the response at the wave vector $\mathbf{q} = 0$ is exactly included beyond TDA. Strictly speaking the calculated response functions go beyond the TDA. As to why this approach is less effective for molecules or larger supercells is also clear: as the cell size increases, the spacing of the reciprocal lattice vectors decreases and singling out one of the densely spaced wave vectors (e.g. $\mathbf{q} = 0$) and treating it exactly becomes less accurate. Hence, for a molecule in a box, results are less accurate for what is commonly called the "TDA" approximation.

The second purpose of the paper was an evaluation of state of the art $\text{GW}+\text{BSE}$ calculations

in comparison to experiment. To date, many BSE calculations are based, on DFT orbitals and DFT one-electron energies, where the unoccupied eigenenergies are shifted to higher energies prior to the BSE calculation. Often the shift is determined by preceding GW calculations or even chosen to reproduce the peak positions in the experimental optical spectrum. Here we have instead performed self-consistent quasiparticle GW calculations (sc-QPGW₀), where the screening in W_0 was determined at the level of density functional theory and the random phase approximation. The predicted spectra are all in excellent agreement with experiment as far as the peak positions are concerned; it is impressive how well parameter-free methods nowadays perform.

8. Macroscopic dielectric function within time-dependent density functional theory - Real time evolution versus the Casida approach*

In 1984, E.K.U Gross suggested an extension to standard density functional theory, which is nowadays referred to as time-dependent density functional theory (TDDFT). [100] It was shown that the fundamental concept of the one-to-one mapping between the one-body density and an external potential also holds in the case of time dependent quantities. In this context, the time-dependent Kohn-Sham equations are set up that include the time-dependent exchange-correlation potential v_{xc} . Although the exact v_{xc} is unknown, there are several approximations to v_{xc} . Among them is the adiabatic local density approximation (ALDA). [143] This approximation yields a computationally tractable working scheme to solve for time-dependent properties such as the response of the ground state to an external perturbation, although the ALDA is known to give rather poor results for the dielectric function, in particular, for large gap materials. It lacks for instance bound excitons. For weak perturbations, the linear response function χ relates the change of the interacting density to an external perturbation. Analogously, the independent particle response function of the Kohn-Sham system χ_{KS} connects the variation of the Kohn-Sham density to the change of the Kohn-Sham potential. Since the Kohn-Sham equations formally yield the exact interacting density and hence the exact density variation, one can link both response functions. This yields the central equation of time-dependent density functional theory $\chi(\omega) = \chi_{KS}(\omega) + \chi_{KS}(\omega) [v_H + f_{xc}(\omega)] \chi(\omega)$, where v_H is the Coulomb kernel and f_{xc} is the frequency dependent exchange-correlation kernel. The kernel is defined as the functional derivative of the exchange-correlation potential w.r.t. the density. For slowly varying densities in time, the already mentioned adiabatic local density approximation is a commonly applied approximation for f_{xc} . It takes into account only the instantaneous density when determining v_{xc} and likewise f_{xc} and results in the static limit of the exchange-correlation kernel for the homogenous electron gas, i.e. $f_{xc}(\omega) \rightarrow f_{xc}$. [143] Gross and Kohn suggested an alternative kernel within the local density approximation that allows to include the frequency dependence of the exchange-correlation kernel. [127] Further approximations have been suggested, such as the nano-quanta kernel [146, 147, 148], the boot strap kernel [149] and kernels based on jellium with a gap. [150]

Casida picked up the idea of Gross. He formulated the density variation in terms of the density matrix response and expressed the equations in terms of an orbital basis. [203] In particular, he showed that it is sufficient to restrict the matrix elements of the density matrix response to

*Based on: T. Sander and G. Kresse, Macroscopic dielectric function within time-dependent density functional theory - Real time evolution versus the Casida approach, *The Journal of Chemical Physics* 146, 064110 (2017).

terms of particle-hole and hole-particle coefficients. The essential outcome is a coupling matrix that relates the variation of the self-consistent part of the Kohn-Sham potential to the density-matrix response. It contains the Hartree kernel and the exchange-correlation kernel and can be seen as an interaction matrix that couples the (resonant) particle-hole and (antiresonant) hole-particle two-orbital states. The poles of the response function correspond to the desired excitation energies, and one finally, has to solve a generalized eigenvalue problem, the Casida equation.[204] It is the key quantity in linear response theory to calculate excitation energies and has the same algebraic structure as the BSE matrix from field theory.[175] The Casida matrix includes matrix elements that couple among the group of resonant/antiresonant two-orbital states, but also between both groups. For computational reasons, it is common practice to neglect the resonant-antiresonant coupling terms in solid state problems. This is known as the Tamm-Dancoff approximation[89, 90]. Such decoupling of resonant and antiresonant terms reduces the computational cost tremendously, as it makes the Casida matrix Hermitian and reduces its dimension by a factor 2. The resulting eigenvalue problem can be solved independently for the positive, as well as for the negative frequency branch. Since the TDA is an additional approximation, results from TDA are generally not exact and differ from the time evolution discussed below.

If one wants to obtain an exact solution, one has to solve the Casida equation exactly without the TDA. The core problem then is that the Casida equation is non-Hermitian. The generalized parallel diagonalization routines provided e.g. by `scaLAPACK`[205] do not exploit the symmetry of the Casida equation and are therefore at least 4 times slower than our present algorithm (diagonalization of a single generalized eigenvalue problem of rank $2N$ instead of diagonalization of two eigenvalue problems of rank N). The full solution of the non-Hermitian Casida equation is thus often determined using custom built iterative methods, which can require significant coding effort.[206, 207] Alternatively, for quantum chemistry problems, the exact solution can be obtained by squaring the original problem.[158, 159] The latter approach has not been used in solid state physics, since it was not obvious how to generalize it to complex Bloch states. Only recently, we have shown that a squared Hermitian problem can be obtained for periodic systems by employing the time inversion symmetry to the group of anti-resonant two-orbital states.[1] This approach now allows to solve for the exact response function without relying on the TDA for solid state problems. Compared to the TDA, the computational effort only doubles and, equally important, standard parallel diagonalization routines can be used to obtain the exact response function.

A completely different approach to obtain response functions is taken by simply following the time evolution of the dipole moment after an external time-dependent delta-function pulse. [201, 208] The frequency dependent polarizability is then extracted from the Fourier transformation of the time evolved dipole moment.[209, 210] For linear properties, the perturbed orbitals are commonly linearized to first order and the free oscillations are followed in time. In order to solve the time-dependent Schrödinger equation, the second order differencing scheme is often applied to propagate the orbitals.[211] The propagation of the orbitals can also be carried out using e.g. predictor-corrected methods [212] or higher order Taylor expansions.[213] Besides the

classical propagation schemes, the time evolution operator can be also calculated by iterative methods, such as the Chebyshev expansion, which has been successfully applied to solid state problems.[208] What all these methods have in common is that they yield the exact polarizability beyond the Tamm-Dancoff approximation. It is commonly assumed that the time-evolution methods are computationally advantageously compared to the Casida approach, as they avoid storing and diagonalizing the Casida matrix. Closely related to time-evolution approaches are methods that determine the response function using Lanczos algorithms. [214, 206] The super operator for propagating the orbital coefficients is equivalent to the time-evolution operator, but instead of calculating the spectrum from a Fourier transformation of evolving dipole moments, the Lanczos algorithm is used to determine the spectral function of the time-evolution operator. According to literature about 2000 evaluations of the time-evolution super-operator are required to obtain converged spectra in this case. This is roughly similar to the number of applications of the time-evolution operator in our present calculations. We thus expect that those method are about as efficient as the time-evolution used here.

The main focus of the present work is to compare the approach suggested by Casida with the time evolution of the orbitals. In particular, we focus on the performance, if the exchange-correlation functional contains a nonlocal exchange contribution. Within the local-density approximation [21] and the generalized gradient approximation (PBE) [37], we test our implemented time evolution code for silicon carbide (SiC), silicon (Si) and the molecule C₆₀ and show that both approaches yield exactly the same spectrum, as expected. Concerning computational requirements, we show that, although time evolution is very efficient for semi-local functionals, time evolution is fairly slow if nonlocal exchange is included. Hence in this case, the Casida approach is computationally clearly preferable.

In the following, we give a brief introduction to the time evolution method in the projected augmented wave (PAW) method and demonstrate how it is related to the Casida equation. Our results are then shown in section 8.3.

8.1. Time evolution method

In the presence of an external perturbation, we know from classical quantum mechanics that the transition probabilities to first order are related to the dipole transition moments. Applying a sharp delta pulse peak $\delta(t)$ to the system in the ground state [201], all optically allowed transitions from the occupied manifold into the unoccupied manifold can be induced. In order to capture the long wave length limit, we consider a spatially constant electric field. This external field, which corresponds to the displacement field $\mathbf{D}$ in Maxwell's equation, is treated in the Coulomb gauge and gives rise to an external potential, which is given by

$$\phi_{\text{ext}}(\mathbf{r}, t) = \lambda \mathbf{r} \cdot \mathbf{D} \delta(t). \quad (8.1)$$

Immediately after the delta pulse, the occupied orbitals obtained from standard first order perturbation theory read

$$|\varphi_i(t=0^+)\rangle = |\varphi_i^0\rangle + \lambda \sum_{a \in \text{virt.}} c_{ai} |\varphi_a^0\rangle, \quad (8.2)$$

with the transition coefficient

$$c_{ai} = \mathbf{D} \cdot \underbrace{\langle \varphi_a^0 | \mathbf{r} | \varphi_i^0 \rangle}_{\boldsymbol{\mu}_{ai}}. \quad (8.3)$$

Here and hereafter we index occupied orbitals and unoccupied (virtual) orbitals as i, j and a, b , respectively and λ denotes the perturbation strength parameter. The superscript 0 indicates the unperturbed single particle orbitals. In Eq. (8.3), $\boldsymbol{\mu}_{ai}$ are the dipole matrix elements. What remains is to follow the free oscillation of the total induced dipole moment. Hence one needs to solve the time-dependent Schrödinger equation. In contrast to the unperturbed solution where the orbitals are simply driven by a phase factor $e^{-\varepsilon_i t}$, the orbitals from Eq. (8.2) contain a small deviation and one seeks a solution of the time-dependent Schrödinger equation that oscillates around the ground state solution. Thus the time-dependent solution can be written as

$$|\varphi_i(t)\rangle = \left\{ |\varphi_i^0\rangle + \lambda |\delta\varphi_i(t)\rangle \right\} e^{-i\varepsilon_i t}, \quad (8.4)$$

with ε_i the eigenvalue of the orbital $|\varphi_i^0\rangle$. The second term on the r.h.s. in Eq. (8.4) contains the time-dependent transition matrix elements $c_{ai}(t)$

$$|\delta\varphi_i(t)\rangle = \sum_{a \in \text{virt.}} c_{ai}(t) |\varphi_a^0\rangle. \quad (8.5)$$

The total dipole moment $\boldsymbol{\mu}$ is given by the expectation value of the dipole operator $\mathbf{r}$

$$\boldsymbol{\mu} = \sum_{i \in \text{occ.}} \langle \varphi_i(t) | \mathbf{r} | \varphi_i(t) \rangle \quad (8.6)$$

and the induced dipole moment $\boldsymbol{\mu}^{(1)}$ is thus in first order given by

$$\boldsymbol{\mu}^{(1)} = \sum_{i \in \text{occ.}} \lambda \left(\langle \varphi_i^0 | \mathbf{r} | \delta\varphi_i(t) \rangle + \langle \delta\varphi_i(t) | \mathbf{r} | \varphi_i^0 \rangle \right). \quad (8.7)$$

From the expression for the induced dipole moment, the polarizability tensor is extracted via a Fourier transformation [215]

$$\alpha_{\gamma\beta}(\omega) = \frac{1}{V} \frac{1}{D_\beta} \int_0^\infty dt \sum_{\substack{a \in \text{virt.} \\ i \in \text{occ.}}} \left(\mu_{ai}^{\gamma*} c_{ai}^\beta(t) + c.c. \right) e^{-i(\omega - i\delta)t}. \quad (8.8)$$

The introduced indices γ and β stand for the individual cartesian x, y, z -directions and δ is an artificial Lorentzian broadening factor to account for a finite time propagation. D_β is the field strength of the delta pulse and V is the unit cell volume. The time evolution needs to be performed three times for the three cartesian directions β , yielding $c_{ai}^\beta(t)$. As the dipole moment

μ_{ai} is ill-defined for periodic systems [79], one makes use of the commutator $[H_{sc}, \mathbf{r}]$ between the self-consistent Hamiltonian and the dipole operator $\mathbf{r}$. Since the local part of the potential commutes with $\mathbf{r}$, the dipole matrix element in Eq.(8.3) can be rewritten as

$$\mu_{ai} = \frac{\langle \varphi_a^0 | [H_{sc}, \mathbf{r}] | \varphi_i^0 \rangle}{\varepsilon_a - \varepsilon_i} = \frac{\langle \varphi_a^0 | \mathbf{p} - [\mathbf{r}, V_{nl}] | \varphi_i^0 \rangle}{\varepsilon_a - \varepsilon_i}. \quad (8.9)$$

Here, $\mathbf{p}$ is the momentum operator and V_{nl} denotes a nonlocal potential, which does not commute with the dipole operator $\mathbf{r}$. [79] In Bloch notation, the indices a and i collates the band and $\mathbf{k}$ -point index ($a \rightarrow c\mathbf{k}$ and $i \rightarrow v\mathbf{k}$). Thus the corresponding matrix elements for the momentum operator reads

$$\langle \varphi_{c\mathbf{k}}^0 | \mathbf{p} | \varphi_{v\mathbf{k}}^0 \rangle = \langle u_{c\mathbf{k}} | i\nabla - \mathbf{k} | u_{v\mathbf{k}} \rangle, \quad (8.10)$$

where $u_{n\mathbf{k}}$ is the cell periodic part, and c and v denote a conduction and valence band, respectively. Matrix elements of the commutator $[\mathbf{r}, V_{nl}]$ need to be evaluated explicitly [see e.g. Ref. [80]]. The corresponding nonlocal terms stem either from the nonlocal part of the pseudopotential or from the nonlocal exchange in the Fock term. For a detailed discussion about the evaluation of the matrix element in Eq.(8.10) within the PAW method, we refer the reader to Ref. [168]. From the solution of the (macroscopic) polarizability tensor the macroscopic dielectric function $\epsilon_M(\omega)$ can be calculated as [126]

$$\epsilon_{\gamma\beta, M}(\omega) = 1 - 4\pi\alpha_{\gamma\beta}(\omega). \quad (8.11)$$

The derivation of this equation assumes that only the Coulomb kernel diverges like $1/q^2$ as one approaches $q \rightarrow 0$. For exchange correlation kernels with a similar $1/q^2$ divergence, this equation needs to be modified, as we discuss in the following paragraph. In density functional perturbation theory, the macroscopic dielectric function is given by the head of the dielectric matrix [62]

$$\epsilon_M^{-1}(\omega) = [1 + v_0\chi(\omega)]_{00}. \quad (8.12)$$

Here and in the following, χ are matrices of two reciprocal wave vectors q, q' , and the subscript 00 implies evaluation of the head, the component at $q, q' \rightarrow 0$. The polarizability matrix $\chi(\omega)$ and the independent particle polarizability $\chi^0(\omega)$ are related by the equation

$$\chi(\omega) = \chi^0(\omega) + \chi^0(\omega) [v + f^{xc}] \chi(\omega), \quad (8.13)$$

or equivalently

$$\chi(\omega)^{-1} = \chi^0(\omega)^{-1} - [v + f^{xc}]. \quad (8.14)$$

In time evolution, the macroscopic field is zero during the time propagation, and only the $q \neq 0$ components of the potential evolve in time. To capture this situation, one needs to separate the Coulomb kernel and the exchange correlation kernel into components $q \rightarrow 0$, call them v_0 and f_0^{xc} , and the rest $\bar{v} + \bar{f} = v + f^{xc} - v_0 - f_0^{xc}$. [62] In time-evolution only the response related to the amputated kernels $\bar{v}$ and $\bar{f}$ are included. Thus the time-evolution yields the head of the

response function $\bar{\chi}(\omega)$ given by

$$\bar{\chi}(\omega) = (\chi^0(\omega)^{-1} - [\bar{v} + \bar{f}])^{-1}. \quad (8.15)$$

The full response needs to be determined by

$$\chi(\omega) = (\bar{\chi}(\omega)^{-1} - [v_0 + f_0^{\text{xc}}])^{-1}. \quad (8.16)$$

Inserting this in Eq. (8.12) yields

$$\epsilon_M^{-1}(\omega) = \left\{ 1 + v_0 [\bar{\chi}(\omega)^{-1} - v_0 - f_0^{\text{xc}}]^{-1} \right\}_{00}. \quad (8.17)$$

After some straightforward algebraic manipulation the macroscopic dielectric function reads

$$\begin{aligned} \epsilon_M(\omega) &= \left[\frac{\bar{\chi}(\omega)^{-1} - v_0 - f_0^{\text{xc}}}{\bar{\chi}(\omega)^{-1} - f_0^{\text{xc}}} \right]_{00} \\ &= \left[1 - v_0 [1 - \bar{\chi}_{00}(\omega) f_0^{\text{xc}}]^{-1} \bar{\chi}_{00}(\omega) \right]. \end{aligned} \quad (8.18)$$

It is easy to see that only the head of $\bar{\chi}$, $\bar{\chi}_{00}$ needs to be known to determine ϵ_M . For an exchange correlation kernel that does not diverge at $q = 0$, the macroscopic dielectric function reduces to Eq.(8.11) ($\alpha(\omega) = \lim_{q \rightarrow 0} \bar{\chi}_{q,q}(\omega)/q^2$, $v_q = 4\pi/q^2$). This is the appropriate form for local or semi-local functionals, which generally lack a divergence as q approaches zero. To make the correction more immediate for the case that the exchange-correlation kernel contributes, one can also Taylor expand the equation yielding:

$$\epsilon_M(\omega) \approx 1 - v_0 \bar{\chi}_{00}(\omega) + \bar{\chi}_{00}(\omega) f_0^{\text{xc}} \bar{\chi}_{00}(\omega). \quad (8.19)$$

If f_q^{xc} diverges like $1/q^2$, a correction term needs to be added to obtain the macroscopic dielectric function (note that $\bar{\chi}_{qq} \propto q^2$). This is reportedly the case for meta-GGA functionals that also depend on the kinetic energy density. However, for the Tao, Perdew, Staroverov, Scuseria (TPSS)[216] functional used here, $f_0^{\text{xc}} \bar{\chi}_{00}(\omega)$ is only of the order of 10^{-3} and can be safely neglected.[128]

8.1.1. Time evolution in the PAW method

In the PAW method,[138, 142] the time-dependent Schrödinger equation involves the overlap operator $\tilde{S} = \mathcal{T}^\dagger \mathcal{T}$ in front of the time derivative [212]

$$i\tilde{S} \frac{\partial}{\partial t} |\tilde{\varphi}(t)\rangle = \tilde{H} |\tilde{\varphi}(t)\rangle. \quad (8.20)$$

The equation above is valid as long as the projection operator $\mathcal{T}$, given by

$$\mathcal{T} = 1 + \sum_j (|\varphi_j^0\rangle - |\tilde{\varphi}_j^0\rangle) \langle \tilde{p}_j|, \quad (8.21)$$

is time independent, i.e. for immobile ions. We adopt the notation of the pseudized one-electron wave functions $|\tilde{\varphi}\rangle$, the pseudized Hamiltonian $\tilde{H}$ and the projector functions $|\tilde{p}_j\rangle$ as in the original paper of Blöchl.[138] Assuming the Hamiltonian to be constant during the time step $t, t + dt$ the time evolution operator then can be cast in the form

$$\hat{U}(t, t + dt) = \tilde{S}^{-\frac{1}{2}} \exp \left(-i \tilde{S}^{-\frac{1}{2}} \tilde{H} \tilde{S}^{-\frac{1}{2}} dt \right) \tilde{S}^{\frac{1}{2}}. \quad (8.22)$$

For a full time-dependent Hamiltonian the corresponding expression is given elsewhere. [210] In order to approximate the time derivative in Eq.(8.20) the second order differencing scheme (SOD) is exploited. It is obtained by Taylor expanding $|\tilde{\varphi}(t)\rangle$ backward and forward in time and subtracting both terms from each other. With a Taylor series expansion of $\hat{U}(t, t + dt)$ one obtains

$$\tilde{S} |\tilde{\varphi}(t+dt)\rangle \approx \tilde{S} |\tilde{\varphi}(t-dt)\rangle - 2i dt \tilde{H} |\tilde{\varphi}(t)\rangle. \quad (8.23)$$

The transition to a finite time step propagation is then understood in terms of a substitution $dt \rightarrow \Delta t$ in Eq.(8.23). This time propagation scheme has the advantage to be symplectic, however, it is obviously not self-starting, since information at two time points is required, although the differential equation is of first order. In Eq.(8.23) the overlap operator causes additional complications. We solve this by projecting onto unoccupied ground state orbitals $\tilde{\varphi}_n^0$ and using the orthogonality relation $\langle \tilde{\varphi}_n^0 | \tilde{S} | \tilde{\varphi}_m^0 \rangle = \delta_{n,m}$. As shown in the previous section, the time evolution of the orbitals is basically driven by the time-dependent dipole transition moments $c_{ia}(t)$. They are easily obtained by projecting the time propagated orbitals onto the unoccupied manifold. Given the expression of Eq.(8.4) and Eq.(8.5) and projecting Eq.(8.23) onto $\langle \varphi_a^0 |$ we have

$$c_{ia}(t_{n+1}) = c_{ia}(t_{n-1}) + 2i\Delta t \langle \varphi_a^0 | \tilde{H} | \varphi_i(t) \rangle. \quad (8.24)$$

The full time evolution algorithm is summarized in the following. To initialize the propagation, the orbitals at time step $t_0 + \Delta t$ need to be calculated. For this purpose, we choose a small interval between t_0 and t_1 and propagate in steps of $\frac{(t_1-t_0)}{N}$. For the very first time propagation from $t_0 \rightarrow t_0 + \frac{\Delta t}{N}$ the time evolution operator is approximated by a first order Taylor series expansion. After that, the propagation is performed on the next $N - 1$ time steps by exploiting Eq.(8.24) until time step t_1 is reached. From now on the remaining computational steps are summarized below:

for $n = 1 \dots t_{\max}$:

- set up orbitals at time step t_n
- update Hamiltonian $\tilde{H} \{ \tilde{\varphi}_i(t_n) \}$
- calculate $\langle \tilde{\varphi}_a^0 | \tilde{H} \{ \tilde{\varphi}_i(t_n) \} | \tilde{\varphi}_i(t_n) \rangle \equiv \delta c_{ia}(t_n)$
- $c_{ia}(t_{n+1}) = c_{ia}(t_{n-1}) + 2i\Delta t \delta c_{ia}(t_n)$.

We note that this algorithm requires no implementation of linearized first order equations, instead the standard ground state routines can be used. One only needs to make certain that the initial c_{ia} are sufficiently large to avoid rounding errors and sufficiently small to remain in the linear

response regime. At least in the VASP code, this is the case for a very wide range with typical initial transition matrix elements of the order of $|c_{ia}| \approx 0.01 \dots 0.1 \text{ e}\text{\AA}$. Increasing or decreasing $|c_{ia}|$ by several orders of magnitude by multiplying with different values of λ did not change the results. As an optimum value, the perturbation parameter was set to $\lambda = 0.05$ for the systems presented here.

A further issue is that even with relatively modest time steps, the oscillation frequencies of $|\tilde{\varphi}(t)\rangle$ are modified compared to the original exact problem. This also affects the dynamical state of the transition matrix element $c_{ai}(t)$ in Eq.(8.8). To show this, we exploit a mode ansatz for the full time dependent solution given in Eq.(8.4). As one seeks an oscillatory solution that deviates from the ordinary time-dependent solution we follow Hedin and Lundqvist [5] and write

$$|\tilde{\varphi}_i(t)\rangle = \left[|\tilde{\varphi}_i^0\rangle + \lambda \sum_{\substack{a \in \\ \text{virt.}}} (X_{ai} e^{-i\Omega t} + Y_{ai}^* e^{i\Omega t}) |\tilde{\varphi}_a^0\rangle \right] e^{-i\varepsilon_i t}. \quad (8.25)$$

This ansatz is motivated by the theorem of Thouless, which yields a condition for collective modes to be stable in the random phase approximation.[217] One finds this ansatz also in other publications [218, 219] that solve for a stable time dependent solution within time-dependent density functional theory. We will also use this ansatz in the next section to show the correspondence to the Casida equation. Basically, this ansatz yields an oscillatory solution with frequency Ω around the time independent solution, where Ω can be identified as an excitation energy. The error of the oscillation frequency can be estimated by inserting this mode ansatz in the second order finite difference equation [Eq.(8.23)] first and subsequently calculating the induced dipole moment from Eq.(8.7). This yields the relation between the numerically obtained frequency Ω' and the exact frequency Ω , as

$$\sin(\Omega' \Delta t) = \Omega \Delta t. \quad (8.26)$$

For very small time steps Δt , the sinus term can be approximated by its argument and thus the approximate oscillation approaches the exact one. To compensate the frequency shift for larger timesteps Δt the Fourier transform in Eq.(8.8) is rescaled by changing the frequency from ω to $\arcsin(\omega t)/t$ in the exponential. Furthermore, the choice of the maximal time step depends on

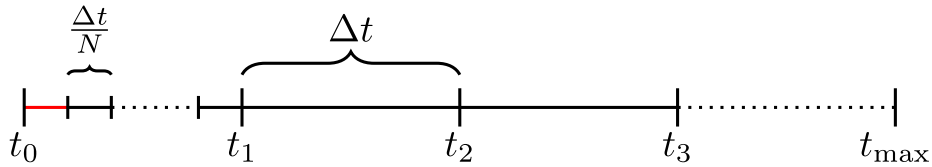


Figure 8.1.: Time step grid on which the coefficients $c(t_n)$ are propagated. The propagation on the red interval $[t_0, t_0 + \frac{\Delta t}{N}]$ is performed with the time evolution operator approximated by a simple first order Taylor expansion. The coefficients on the remaining black intervals are calculated with the aid of Eq.(8.23).

the maximum transition energies $E_{\max}$ considered and needs to satisfy the stability condition

$$\Delta t \leq \hbar/E_{\max}. \quad (8.27)$$

8.1.2. Connection to the Casida equation

Instead of solving the time-dependent Schrödinger equation, the von Neumann equation for the density matrix can be solved alternatively. Considering a noninteracting fermionic many-particle system, the associated density matrix $\rho(\mathbf{r}, \mathbf{r}', t)$ can be written in terms of a set of orthonormal orbitals $\{\varphi_j(\mathbf{r}, t)\}$ as

$$\rho(\mathbf{r}, \mathbf{r}', t) = \sum_{j \in \text{occ.}} \varphi_j(\mathbf{r}, t) \varphi_j^*(\mathbf{r}', t). \quad (8.28)$$

These orbitals are solutions of a self-consistent (sc) Hamiltonian $H_{\text{sc}}(\mathbf{r}, \mathbf{r}', t)$ which we additionally extend to include a fraction of nonlocal exchange

$$\begin{aligned} i \frac{\partial}{\partial t} \varphi_i(\mathbf{r}, t) &= H_{\text{sc}}(\mathbf{r}, \mathbf{r}', t) \varphi_i(\mathbf{r}, t) \\ &= [H(\mathbf{r}, \mathbf{r}', t) + c_x H_{\text{nl}}(\mathbf{r}, \mathbf{r}', t)] \varphi_i(\mathbf{r}, t). \end{aligned} \quad (8.29)$$

Note that we have disregarded the overlap operator here and in the following to simplify the notation. The one-electron part $H(\mathbf{r}, \mathbf{r}', t)$ contains the kinetic energy operator and the potential due to the nuclei denoted by h , the Hartree potential V_{H} and the exchange-correlation potential V_{xc} and is defined as

$$\begin{aligned} H(\mathbf{r}, \mathbf{r}', t) &= \delta(\mathbf{r} - \mathbf{r}') [h(\mathbf{r}) + V_{\text{H}}(\mathbf{r}, t) \\ &\quad + V_{\text{xc}}^{\text{DFA}}(\mathbf{r}, t) + (1 - c_x) V_{\text{x}}^{\text{DFA}}(\mathbf{r}, t)]. \end{aligned} \quad (8.30)$$

In the equation above, the exchange-correlation potential $V_{\text{xc}}^{\text{DFA}}$ and the exchange potential $V_{\text{x}}^{\text{DFA}}$ are given in a density functional approximation (DFA). The remaining nonlocal part H_{nl} of Eq.(8.29) is represented by the Fock operator, i.e.

$$H_{\text{nl}}(\mathbf{r}, \mathbf{r}', t) = \frac{\rho(\mathbf{r}, \mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (8.31)$$

If we set the parameter c_x to zero we obtain the time-dependent Kohn-Sham Hamiltonian and thus control the amount of exact exchange by c_x which is chosen to be 1/4 in our hybrid-DFT calculations. The corresponding equation of motion for the density matrix can be written in position space as

$$i \frac{\partial}{\partial t} \rho(\mathbf{r}, \mathbf{r}', t) = \int d\mathbf{r}'' [H_{\text{sc}}(\mathbf{r}, \mathbf{r}'', t) \rho(\mathbf{r}'', \mathbf{r}', t) - \rho(\mathbf{r}, \mathbf{r}'', t) H_{\text{sc}}(\mathbf{r}'', \mathbf{r}', t)]. \quad (8.32)$$

In a matrix representation, the density matrix is rewritten as

$$\rho(\mathbf{r}, \mathbf{r}', t) = \sum_{m,n} \varphi_m^0(\mathbf{r}) \varphi_n^{0*}(\mathbf{r}') \rho_{mn}(t), \quad (8.33)$$

while its matrix elements are given in terms of the stationary orbitals of Eq.(8.29)

$$\rho_{mn}(t) = \int d\mathbf{r} d\mathbf{r}' \varphi_m^{0*}(\mathbf{r}) \varphi_n^0(\mathbf{r}') \rho(\mathbf{r}, \mathbf{r}', t). \quad (8.34)$$

We use the indices m, n to denote all occupied and unoccupied orbitals. By use of Eq.(8.33) the equation of motion [Eq.(8.32)] can be cast into the form

$$i \frac{\partial}{\partial t} \rho_{mn}(t) = \sum_{\substack{l \in \\ \text{occ., virt.}}} H_{ml}(t) \rho_{ln}(t) - H_{ln}(t) \rho_{ml}(t), \quad (8.35)$$

where matrix elements of the sc Hamiltonian are defined as

$$H_{ml}(t) = \int d\mathbf{r} d\mathbf{r}' \varphi_m^{0*}(\mathbf{r}) H_{\text{sc}}(\mathbf{r}, \mathbf{r}', t) \varphi_l^0(\mathbf{r}'). \quad (8.36)$$

By linearizing the density matrix, the equation of motion for the response of the density matrix $\rho^{(1)}$ is given by [5]

$$i \frac{\partial}{\partial t} \rho_{mn}^{(1)}(t) = (\varepsilon_m - \varepsilon_n) \rho_{mn}^{(1)}(t) + (f_n - f_m) H_{mn}^{(1)}(t) \quad (8.37)$$

or equivalently in the frequency domain [203, 220]

$$\rho_{mn}^{(1)}(\omega) = \frac{f_m - f_n}{\varepsilon_m - \varepsilon_n - \omega} H_{mn}^{(1)}(\omega). \quad (8.38)$$

In the equation above, the superscript (1) means the perturbed part of the sc Hamiltonian, f_n are the Fermi weights and the ε_n are the eigenvalues of the corresponding orbitals $\varphi_n^0(\mathbf{r})$. For an explicit expression of the matrix elements $H_{mn}^{(1)}$ in Eq.(8.38) w.r.t. the local Hartree potential and the exchange-correlation potential, we refer the reader to Ref. [203, 220]. The corresponding nonlocal term $H_{\text{nl},mn}^{(1)}$ is derived in the appendix [see Eq.(K.4)].

We now briefly discuss the relation to the time propagation discussed before. Equation (8.35) is of course exactly equivalent to the equation used for the propagation of the orbital coefficients. Equation (8.35) describes the oscillations of the density matrix driven by the sc Hamiltonian of Eq.(8.29), in the absence of an external potential. This is equivalent to time evolution, where the initial action of the external potential ϕ_{ext} only induced transitions from the occupied manifold into the unoccupied manifold spanned by the set of stationary orbitals φ_i^0 of the unperturbed Hamiltonian. After the pulse, the external potential is zero, and the changes of the Hamiltonian are then simply given by the time dependence of the sc Hamiltonian induced by the time-dependent density matrix [compare Eq.(8.29) and (8.37)].

To obtain the final Casida equation, one can use a mode ansatz, as discussed in this paragraph. By virtue of Eq.(8.38), the solution of the density matrix response turns into a self-consistent time-dependent problem. For gaped systems it is convenient to consider the matrix elements $\rho_{ai}^{(1)}$ or $\rho_{ia}^{(1)}$ only, which results in the common 'electron-hole' and 'hole-electron' notation. By exploiting the mode ansatz of Eq.(8.25), the Fourier transform of the first order density matrix response yields for a single mode with frequency Ω

$$\begin{aligned} \rho^{(1)}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\substack{i \in \text{occ} \\ a \in \text{virt}}} \Big\{ & \varphi_i(\mathbf{r}) [X_{ai}^* \delta(\omega - \Omega) + Y_{ai} \delta(\omega + \Omega)] \varphi_a^*(\mathbf{r}') \\ & + \varphi_i^*(\mathbf{r}') [X_{ai} \delta(\omega + \Omega) + Y_{ai}^* \delta(\omega - \Omega)] \varphi_a(\mathbf{r}) \Big\}. \end{aligned} \quad (8.39)$$

It is evident that the density matrix response consists of two modes corresponding to $e^{i\Omega t}$ and $e^{-i\Omega t}$ which results in the corresponding delta peaks $\delta(\omega - \Omega)$ and $\delta(\omega + \Omega)$ in the frequency domain, respectively. One can insert the ansatz Eq.(8.39) into Eq.(8.38) for either the positive or negative frequency but needs to consider both, $\rho_{ai}^{(1)}$ and $\rho_{ia}^{(1)}$. For the positive mode one obtains a coupled matrix equation given by:

$$\begin{aligned}\Omega X_{ai}^* &= (\varepsilon_a - \varepsilon_i) X_{ai}^* + \sum_{j,b} \left\{ \langle ib|K|aj\rangle - c_x \langle ib|v|ja\rangle \right\} X_{bj}^* + \left\{ \langle ij|K|ab\rangle - c_x \langle ij|v|ba\rangle \right\} Y_{bj}^* \\ -\Omega Y_{ai}^* &= (\varepsilon_a - \varepsilon_i) Y_{ai}^* + \sum_{j,b} \left\{ \langle ab|K|ij\rangle - c_x \langle ab|v|ji\rangle \right\} X_{bj}^* + \left\{ \langle aj|K|ib\rangle - c_x \langle aj|v|bi\rangle \right\} Y_{bj}^*.\end{aligned}\tag{8.40}$$

This can be rewritten in a more compact form as

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}^* \\ \mathbf{Y}^* \end{pmatrix} = \Omega \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}^* \\ \mathbf{Y}^* \end{pmatrix},\tag{8.41}$$

where matrix elements of the submatrices $\mathbf{A}$ and $\mathbf{B}$ read

$$A_{ai,bj} = (\varepsilon_a - \varepsilon_i) \delta_{i,j} \delta_{a,b} + \langle ib|K|aj\rangle - c_x \langle ib|v|ja\rangle\tag{8.42}$$

$$B_{ai,jb} = \langle ij|K|ab\rangle - c_x \langle ij|v|ba\rangle.\tag{8.43}$$

Here, the kernel K is the sum of the Coulomb kernel $v(\mathbf{r}, \mathbf{r}') = |\mathbf{r} - \mathbf{r}'|^{-1}$ and the exchange-correlation kernel $f_{xc}(\mathbf{r}, \mathbf{r}')$, and the corresponding matrix elements of K and of the Coulomb kernel v have the general form

$$\langle mn|g|pq\rangle \equiv \int d\mathbf{r} d\mathbf{r}' \varphi_m^*(\mathbf{r}) \varphi_n^*(\mathbf{r}') g(\mathbf{r}, \mathbf{r}') \varphi_p(\mathbf{r}) \varphi_q(\mathbf{r}').\tag{8.44}$$

Within the adiabatic formulation of TDDFT, the xc kernel is local in time and hence frequency independent. In this commonly applied approximation we have

$$f_{xc}(\mathbf{r}, \mathbf{r}') \approx \frac{\delta^2 \{E_c^{\text{DFA}} + (1 - c_x) E_x^{\text{DFA}}\}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} + c_x \frac{\delta^2 E_x^{\text{exact}}}{\delta^2 \rho(\mathbf{r}, \mathbf{r}')}. \tag{8.45}$$

Here, the density $\rho(\mathbf{r})$ is the diagonal of the density matrix $\rho(\mathbf{r}) \equiv \rho(\mathbf{r}, \mathbf{r})$. The second term of the r.h.s of Eq.(8.45) involves the second derivative of the exact exchange energy w.r.t the density matrix and gives rise to the last term in Eq.(8.42) and Eq.(8.43). An algebraic equivalent formulation of Eq.(8.41) follows for the conjugated eigenvector $(\mathbf{Y}, \mathbf{X})$ with eigenvalues $-\Omega$. The solution of the generalized eigenvalue problem [Eq.(8.41)] yields the desired excitation energies. To solve for the eigenvalues Ω , we proceed as in our previous publication.[1] In contrast to quantum chemistry, where the matrices $\mathbf{A}$ and $\mathbf{B}$ are real valued, the matrices are complex albeit Hermitian in solid state theory. Since the matrix elements of $\mathbf{A}$ and $\mathbf{B}$ are expressed in terms of Bloch functions, the orbital index now contains the band and $\mathbf{k}$ point index, i.e. $(n\mathbf{k})$. This allows to apply the time inversion symmetry where to every Bloch orbital $\varphi_{n\mathbf{k}}$ a complex

conjugated orbital $\varphi_{n-\mathbf{k}}^*$ is associated, both having the same orbital energy. We exploit this time inversion and can thus rewrite the complex conjugated matrices in Eq.(8.41) by means of $\mathbf{B}^* \rightarrow \mathbf{B}$ and $\mathbf{A}^* \rightarrow \mathbf{A}$, i.e. we replace the orbital $\varphi_{n\mathbf{k}}$ by $\varphi_{n-\mathbf{k}}^*$ in the lower and right part of the square matrix.[1] What remains is to solve the following now Hermitian but generalized eigenvalue problem

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X}^* \\ \mathbf{Y}^* \end{pmatrix} = \Omega \begin{pmatrix} \mathbb{1} & 0 \\ 0 & -\mathbb{1} \end{pmatrix} \begin{pmatrix} \mathbf{X}^* \\ \mathbf{Y}^* \end{pmatrix}. \quad (8.46)$$

We note that this eigenvalue problem can also be solved in terms of the eigenvector $(\mathbf{Y}, \mathbf{X})$ at the frequency $-\Omega$. This is however redundant, since both vectors, i.e. $(\mathbf{Y}, \mathbf{X})$ and $(\mathbf{X}^*, \mathbf{Y}^*)$ yield the same algebraic eigenvalue problem.

The final step is to rephrase the generalizes eigenvalue problem as a quadratic Hermitian eigenvalue problem that can be solved efficiently using available linear algebra packages. From Eq.(8.46), an equivalent quadratic eigenvalue problem can be derived and reads

$$\left[(\mathbf{A} - \mathbf{B})^{\frac{1}{2}} (\mathbf{A} + \mathbf{B}) (\mathbf{A} - \mathbf{B})^{\frac{1}{2}} \right] (\mathbf{A} - \mathbf{B})^{-\frac{1}{2}} (\mathbf{X}^* + \mathbf{Y}^*) = \Omega^2 (\mathbf{A} - \mathbf{B})^{-\frac{1}{2}} (\mathbf{X}^* + \mathbf{Y}^*). \quad (8.47)$$

A well documented and a detailed derivation of Eq.(8.47) can be found e.g. in Ref. [159, 158, 1]. From Eq.(8.46) one reads off that the eigenvectors form a supervector: while $\mathbf{X}^*$ holds particle-hole matrix elements of the density matrix response $\rho^{(1)}$, $\mathbf{Y}^*$ holds the hole-particle elements, respectively. At this point, some further comments are appropriate concerning the solution of Eq.(8.47). First of all, if the eigenvalues Ω are real the oscillatory ansatz in Eq.(8.25) represents a stationary oscillation about the ground state.[221, 5] Secondly, the matrix $(\mathbf{A} - \mathbf{B})$ needs to be positive definite so that its square root is well defined and single valued. Even more, positive definiteness of $(\mathbf{A} \pm \mathbf{B})$ guarantees a stable reference state from which excitations are considered and hence yields positive definite eigenvalues Ω . [222] The condition of positive definiteness of $(\mathbf{A} - \mathbf{B})$ is easy to establish in the case of TDDFT, because with our ansatz (time inversion symmetry) the matrix $(\mathbf{A} - \mathbf{B})$ is only diagonal with elements $\varepsilon_a - \varepsilon_i$ and hence positive definiteness is guaranteed for pure density functionals. For hybrid functionals, positive definiteness is not generally provable, but in practice commonly observed.

The final quantity of interest is the long wave length limit of the polarizability, *i.e.* the macroscopic dielectric which is given by [1]

$$\begin{aligned} \epsilon_M(\omega) = & 1 - \frac{4\pi e^2}{V} \sum_{\Lambda} \left(\frac{1}{\omega - \Omega_{\Lambda}} - \frac{1}{\omega + \Omega_{\Lambda}} \right) \times \\ & \times \left\{ \sum_{\mathbf{k}} \sum_{c,v} w_{\mathbf{k}} \hat{\mathbf{q}} \left[\mu_{cv,\mathbf{k}} X_{\Lambda}^{*(i,a)\mathbf{k}} + \mu_{cv,-\mathbf{k}}^* Y_{\Lambda}^{*(a,i)-\mathbf{k}} \right] \right\} \times \left\{ c.c. \right\}, \end{aligned} \quad (8.48)$$

where $\mu_{cv,\mathbf{k}}$ denotes the matrix dipole element as defined by Eq.(8.9) with the conduction band index c , the valence band index v and the $\mathbf{k}$ -point index $\mathbf{k}$, respectively. The unit vector $\hat{\mathbf{q}}$ indicates the direction of the applied external field $\mathbf{D}$. Furthermore, by the index $-\mathbf{k}$ we denote the dipole matrix element calculated with the corresponding Bloch orbital at the negative $\mathbf{k}$ vector, Λ is the eigenvector index of Eq.(8.46), $w_{\mathbf{k}}$ denotes the $\mathbf{k}$ -point weight and V is the

volume of the unit cell. This equation is the exact analog of (8.11), which relates to the fact that solving the Casida equation or the time-evolution equation is done in the absence of a macroscopic field, as already discussed a few lines above. This point is also discussed in detail in Ref. [1].

8.2. Computational complexity

The computational requirements are summarized in Tab. 8.1. The time evolution method behaves in most parts as a conventional ground state calculation. Application of the Hamiltonian on the occupied manifold scales linear in the number of $\mathbf{k}$ -points $N_{\mathbf{k}}$ and the number of occupied orbitals N_{occ} . In most cases, the cost for each evaluation of the Hamiltonian is dominated by the cost for Fast-Fourier transformations ($N_{\text{plw}} \ln N_{\text{plw}}$). There is one point requiring additional compute time compared to groundstate calculations: we evaluate the update of the orbital coefficients $\delta c_{ia}(t_n)$ (compare Eq. (8.24) and schematics following Eq. (8.24)) by projection onto the virtual orbitals. Hence the code needs to pre-calculate and store a certain number of unoccupied orbitals and project onto these orbitals in each step. However, within the linear response regime, it is commonly sufficient to use a fairly small number of virtual orbitals, typically as many or twice as many as the occupied orbitals. With present high performance basic linear algebra subroutines (BLAS), the cost for this projection is fairly modest for the system sizes considered here. Alternatively one could also invert the overlap operator as was done in Ref. [223] reducing the scaling of the projection step for very large systems. Overall, for the system sizes considered here, one step in the time propagation requires half the compute time of one step in groundstate calculations, as the Hamiltonian is only applied once to each orbital in the TE, whereas VASP usually applies the Hamiltonian two to three times per step and orbital for groundstate calculations.

Table 8.1.: Memory and compute time of the time evolution method and the Casida approach. For the time evolution, the compute time for hybrid functionals increases, because of the need to evaluate the nonlocal exchange. $N_{\mathbf{k}}$ is the number of $\mathbf{k}$ -points, N_{occ} and N_{virt} the number of occupied and virtual (unoccupied) orbitals, and N_{plw} the number of plane waves.

	Time evolution	Casida
Memory	$N_{\mathbf{k}} \times (N_{\text{occ}} + N_{\text{virt}}) N_{\text{plw}}$	$(N_{\mathbf{k}} \times N_{\text{occ}} \times N_{\text{virt}})^2$
Compute time	$N_{\mathbf{k}} \times N_{\text{occ}} \times N_{\text{plw}} \ln N_{\text{plw}} +$ $+ N_{\mathbf{k}} \times N_{\text{occ}} \times N_{\text{virt}} \times N_{\text{plw}}$	$(N_{\mathbf{k}} \times N_{\text{occ}} \times N_{\text{virt}})^3$
Nonlocal exchange	$+ N_{\mathbf{k}}^2 \times N_{\text{occ}}^2 \times N_{\text{plw}} \ln N_{\text{plw}}$	-

Contrary to this, the cost for the Casida approach in the present VASP implementation is dominated by the diagonalization of the Casida matrix, which has a dimension of $N_{\text{rank}} = N_{\mathbf{k}} \times N_{\text{occ}} \times N_{\text{virt}}$. Storing the matrix requires N_{rank}^2 entries, whereas the diagonalization scales cubically with the matrix rank N_{rank}^3 . If we consider that the number of $\mathbf{k}$ -points can be usually reduced when the number of atoms N in the box increases, we find that the total compute time increases quadratic with N for TE (disregarding the projection step), and cubically with N for

Casida's approach. This suggests that time evolution should usually be more efficient, and as we will discuss below this is always the case for density functional theory calculations. For hybrid functionals, the TE, however, requires one to evaluate the nonlocal exchange in each time step. The cost for this step is quadratic in the number of $\mathbf{k}$ -points and occupied orbitals as shown in the last line of Tab. 8.1. Obviously this does not worsen the scaling with the number of atoms N , which is in total still quadratic for TE. However, if many $\mathbf{k}$ -points are included the compute cost of hybrid functionals is usually two, sometimes even three, orders of magnitude larger than for local or semi-local functionals. We hence, expect that TE will be inefficient for small systems, ultimately outperforming the Casida approach only for very large system sizes. We note that the additional compute cost for the Casida approach for hybrid functionals is modest: essentially the setup of the $\mathbf{A}$ and $\mathbf{B}$ matrices becomes about a factor two more time-consuming, since additional integrals need to be calculated.

Before continuing, we note that many time evolution implementations forgo on the projection step, and instead simply propagate the orbitals using some higher order difference scheme or the split operator approach.[210, 224] This certainly has several advantages: the computational complexity is reduced, and the scaling with system size is improved. Furthermore, results are from the outset essentially basis set converged without the need to check for convergence with respect to the number of virtual orbitals. However, without projection the numerical stability significantly worsens and the time steps need to be chosen much smaller than in the present implementation. At least for solids, reasonable convergence with respect to the number of virtual orbitals is often already achieved by including as many virtual as occupied orbitals. Then the projection step is very cheap, and our present implementation efficient. Certainly the situation is different for molecules in a box, but in that specific case, Gaussian basis set codes are usually much more efficient than plane wave implementations, and these type of systems are therefore not the main focus of the plane wave code VASP. Nevertheless, below we will demonstrate that good results can be obtained with reasonable computational effort even for such cases.

8.3. Results

In this section, we compare the results for the macroscopic dielectric function from the solution of the Casida equation against the results of the time evolution of the orbitals. We apply both methods to the bulk systems silicon (Si) and silicon carbide (SiC) and to the molecule carbon C_{60} . The crucial point is to discuss the computational efficiency of the time evolution method compared to the direct diagonalization in the Casida method.

8.3.1. Numerical details

First of all, we shall give some details about the computational aspects. All calculations have been performed with the plane-wave code VASP using the PAW method to calculate all electron orbitals and energies. When we work within the framework of density functional theory, exchange and correlation effects are approximated by either the local-density approximation (LDA) [21] or the generalized gradient approximation (PBE).[37] The latter one is exploited for silicon

Table 8.2.: Three different $\mathbf{k}$ -point grids are used for each of the applied exchange and correlation functionals. All grids are shifted off- Γ by $\mathbf{s} = (1/12, 3/12, 5/12)$.

LDA/PBE	hybrid-LDA/hybrid-PBE	TPSS
$12 \times 12 \times 12$	$8 \times 8 \times 8$	$24 \times 24 \times 24$

and carbon C_{60} , whereas the LDA is applied for silicon carbide. In order to include also exact exchange, we extend our calculations and employ the hybrid functionals hybrid-PBE (PBEh)[225] and a similar hybrid-LDA.[225] As a third group of density functionals, meta-GGA functionals that additionally depend on the kinetic energy density are used. These functionals seem to be promising to give improved results for optical properties.[128] In this work, we employ the Tao, Perdew, Staroverov, Scuseria (TPSS) functional[216] within the time evolution method.

For the bulk systems silicon carbide and silicon, the Brillouin zone was sampled by three different $\mathbf{k}$ -point grids shifted off- Γ as shown in table 8.2. In the case of carbon C_{60} , the molecule was put into a simple cubic supercell surrounded by vacuum of about $5\text{\AA}$ to minimize the overlap of the orbitals with adjacent molecules. Its structural parameters have been relaxed using a hard pseudo-potential that gives an all-electron precision. As we aim for the calculation of the macroscopic dielectric function from Eq.(8.11) and Eq.(8.48), we first perform a DFT ground state calculation for all three different exchange and correlation functionals and obtain the desired Kohn-Sham orbitals and corresponding Kohn-Sham energies. These quantities then serve as input to calculate the macroscopic polarizability using the time evolution method and the Casida equation, respectively. Concerning the computational effort, the Casida method requires to set up the matrices $\mathbf{A}$ and $\mathbf{B}$ introduced in section 8.1.2. Their dimension equals the number of occupied bands times the number of unoccupied bands times the number of $\mathbf{k}$ -points which defines the system size in the Casida approach. Thus the memory demand increases quadratically with the system size and hence illustrates that this method might require a prohibitive amount of memory. On the other hand, modern multicore, multiprocessor systems often have a huge amount of memory. This can be used efficiently if the matrices are stored distributed, as it is done in VASP, and if parallel diagonalization routines provided by linear algebra packages, such as scaLAPACK [205], are employed.

In contrast to this, the time evolution method involves calculating the action of the Hamiltonian on each of the occupied orbitals, projection onto the unoccupied groundstate orbitals, and a propagation of the density matrix. The memory demand increases linear with the number of bands, the number of plane waves and the number $\mathbf{k}$ -points. This means that the memory demand and the compute time per time step is roughly comparable to an ordinary DFT calculation. To initialize the time propagation, we apply a spatially constant external field separately in all three cartesian directions which concomitantly breaks the crystal symmetry. The action of the external potential onto the electronic part is calculated from Eq.(8.2). Subsequently the time propagation is then carried out on an equally spaced time grid with a total simulation time of 33 fs. We have chosen the time steps Δt to be $1/2\Delta t_{\text{max}}$, where the maximum time step depends on the maximum transition energy [see Eq.(8.27)].

Table 8.3.: Total computational time for solving the Casida equation versus the time evolution (TE) simulation. The numbers below are given in minutes and are obtained from the wall clock time multiplied by the number of CPU cores. For each xc-functional a different $\mathbf{k}$ -point grid is used, as shown in Table 8.2 and by the numbers in brackets in the third line. A Γ -only $\mathbf{k}$ -point grid is used for C_{60} .

$\mathbf{k}$ -points	DFT	hybrid-DFT	TPSS
	TE/Casida ($12 \times 12 \times 12$)	TE/Casida ($8 \times 8 \times 8$)	TE ($24 \times 24 \times 24$)
SiC	179/5 793	19 082/173	5 407
Si	183/8 800	17 406/279	5 366
C_{60}	13 845/25 453	112 637/30 861	26 238

8.3.2. Density functional theory

Our results for silicon carbide (SiC), silicon (Si) and carbon C_{60} are shown in the Fig. 8.2, 8.3 and 8.4. To cover a sufficient spectral range of the dielectric function the transition space is made up by 4 occupied bands N_{occ} and 8 unoccupied bands N_{unocc} for silicon carbide and silicon. This allows to include transition energies up to 28 eV. For carbon C_{60} we include transition pairs between 120 occupied bands and 600 unoccupied bands which covers transition energies up to 50 eV. In turn, the maximum transition energy yields a maximum time step Δt_{max} of about 0.023 fs for silicon carbide and silicon and a maximum time step of about 0.011 fs for carbon C_{60} . For a total simulation time of 33 fs this yields 1400 time steps for silicon and silicon carbide and 3000 time steps for carbon C_{60} . The time steps have been chosen to converge the spectra w.r.t. peak positions as the resolution of the transition frequencies depends on the total simulation time. In Fig. 8.2 the results for the macroscopic dielectric function for silicon carbide are shown. First of all, we can observe a perfect agreement of the peak positions as well as of the peak intensities obtained from both methods within the local density approximation. In the case of silicon, where we have used the PBE functional, the agreement is also very satisfactory as demonstrated in Fig. 8.3. Slight disagreement of the intensities is found which is due to different implementations of the density gradient corrections of the PBE functional in the Casida approach and in the time evolution method. Clearly, in comparison with the experiment, the calculated spectrum is unsatisfying with respect to the peak intensities as well as the peak positions, which are red-shifted by about 0.48 eV. This shift has been added to the experimental data to match the peak positions in Fig. 8.3. The same qualitative results comparing the time evolution method and the Casida approach are obtained also for carbon C_{60} as presented in Fig. 8.4. Of particular interest is the comparison of the total computational time. For both methods, VASP was executed in parallel and the best computational setup was chosen to achieve optimal efficiency for the number of used cores. From Tab. 8.3 one reads off the total computational time. With the Casida method chosen as reference value, the time evolution method takes only about 3% for SiC and about 2% for Si of the total reference time. A less pronounced difference in the total computational time is found for carbon C_{60} which is about 54% of the reference time of the Casida method.

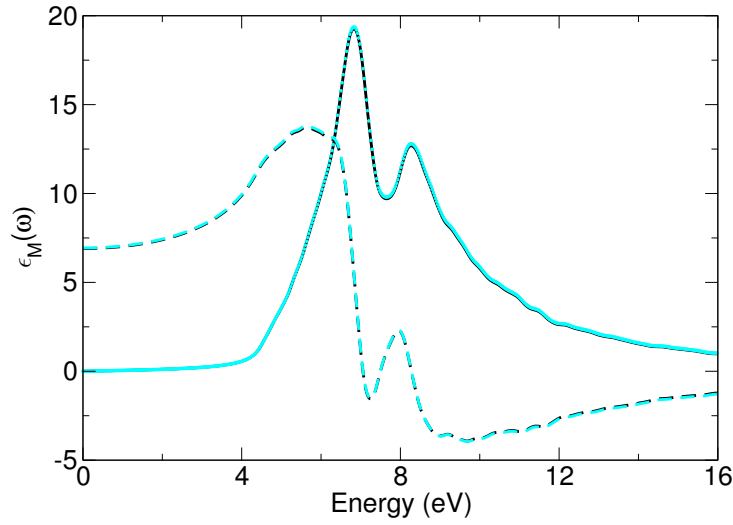


Figure 8.2.: Real (broken) and imaginary (full and dotted) part of the macroscopic dielectric function $\epsilon_M(\omega)$ of silicon carbide (SiC) obtained from the solution of the Casida matrix (black broken/black) and from the time evolution of the orbitals (cyan broken/cyan dotted). The exchange-correlation functional is approximated using the local-density approximation (LDA) and a $12 \times 12 \times 12$ $\mathbf{k}$ -point grid shifted off- Γ is used.

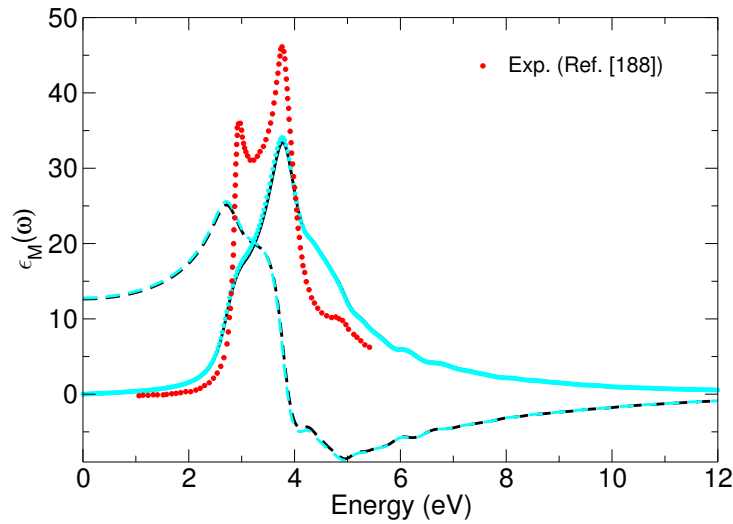


Figure 8.3.: Real and imaginary part of the macroscopic dielectric function $\epsilon_M(\omega)$ of silicon (Si). Color coding as in Fig. 8.2. The generalized gradient approximation PBE is applied to approximate the exchange and correlation functional and a $12 \times 12 \times 12$ $\mathbf{k}$ -point grid shifted off- Γ is used. Experimental data (red dots) are taken from Ref. [188] and are additionally red-shifted by 0.48 eV.

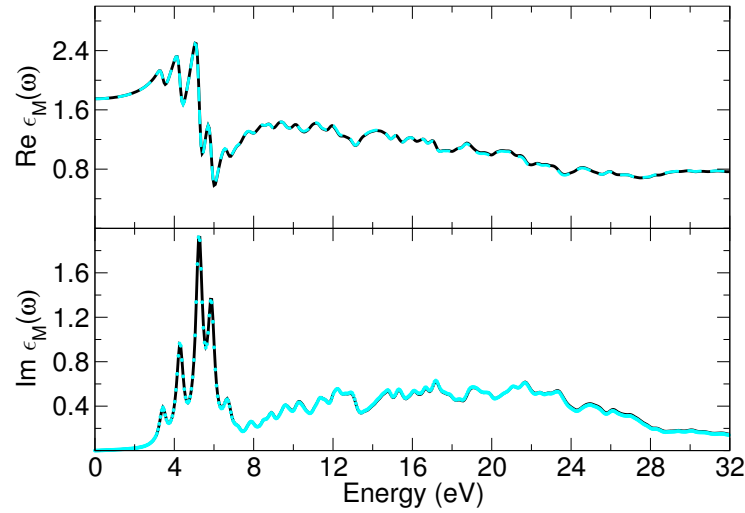


Figure 8.4.: Real and imaginary part of the macroscopic dielectric function $\epsilon_M(\omega)$ of carbon C_{60} . Color coding as in Fig. 8.2. The PBE functional is applied.

8.3.3. Hybrid functionals

In the following, we present the results for the macroscopic dielectric function now including an admixture of exact exchange to the exchange-correlation functional. The exchange energy functional includes 1/4 of the exact exchange and 3/4 of the density functional theory exchange of LDA or PBE, respectively. All calculations were performed on a shifted $8 \times 8 \times 8$ $\mathbf{k}$ -point grid. Using more $\mathbf{k}$ -points would have made the time-evolution calculations computationally prohibitive.

Again we find overall excellent agreement of the macroscopic dielectric function for the two theoretical methods for all three systems as shown in Fig. 8.5, 8.6 and 8.7. The inclusion of exact exchange clearly improves the spectrum of silicon by enhancing the first peak that is only visible as a shoulder at around 3 eV in the corresponding DFT spectrum. The intensity of the second peak at around 4 eV changes only slightly. The calculated spectrum, though, is still red-shifted by about 0.23 eV with respect to the experimental data. This shift has been taken into account in Fig. 8.6 by red-shifting the experimental spectrum by the same amount. The effect of the additional exchange contribution, however, is recognizable in the spectrum as the two main peaks E_1 and E_2 become clearly resolved. For silicon carbide, the peak around 7 eV exhibits a gain of intensity at the expense of a reduced intensity for the peak around 9 eV. Carbon C_{60} also shows a gain of intensity for the peak around 4 eV, whereas the second main peak at about 5 eV becomes less pronounced. Due to the additional computational cost caused by the exact exchange treatment in the time evolution case, solving the Casida equation obviously is now clearly more favorable. The explicit calculation of the exchange part scales quadratic with the number of $\mathbf{k}$ -points and its repetitive calculation within the time evolution increases the total computational time tremendously. This is also reflected by the numbers given in table 8.3. With the Casida method as reference, the time evolution method is slower by a factor of about 110 for silicon carbide, and is about 60 times slower for silicon. For carbon C_{60} the computational

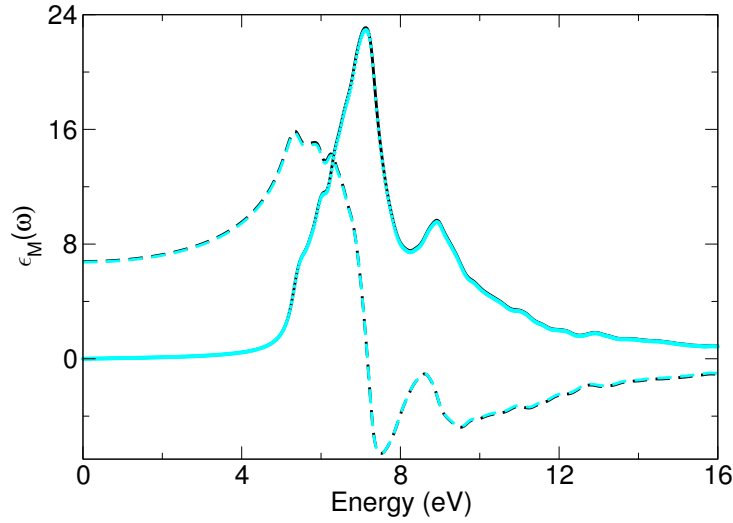


Figure 8.5.: Real and imaginary part of the macroscopic dielectric function $\epsilon_M(\omega)$ of silicon carbide (SiC) calculated on a shifted $8 \times 8 \times 8$ $\mathbf{k}$ -point grid. A hybrid density functional composed of $1/4$ of the exact exchange E_x and $3/4$ of the exchange of the LDA density functional E_x^{LDA} is used. The LDA correlation is fully included. Color coding as in Fig.(8.2)

performance is about 4 times slower compared to the solution of the Casida method. In this case, the increase in compute time from DFT to the hybrid functional for the time evolution algorithm is only about a factor 10, which is typical for single $\mathbf{k}$ -point calculations. What makes exchange so expensive in solids is the double-loop over $\mathbf{k}$ -points.

8.3.4. TPSS

An advantage of the time evolution method is that frequency dependent properties can be calculated for any functional for which groundstate properties are computable, since second derivatives of the exchange-correlation functional do not need to be implemented. In the following section, we present results for the macroscopic dielectric function where the exchange-correlation functional is now approximated by the meta-GGA functional TPSS.[216] For this functional, the time evolution method has been applied exclusively and the Brillouin zone was sampled by a shifted $24 \times 24 \times 24$ $\mathbf{k}$ -point grid. In contrast to the (semi-)local approximations (GGA) LDA, meta-GGA functionals incorporate a $1/q^2$ divergence of the exchange-correlation kernel f_{xc} in the long wave length limit $q \rightarrow 0$. [128] This divergence stems from the nonlocality of $f_{xc}(\mathbf{r}, \mathbf{r}')$ and has been suggested to reproduce excitonic effects in the optical spectrum. The nonlocality vanishes completely in the local-density approximation. [147, 226] In the light of these arguments, our TPSS results for SiC, Si and carbon C_{60} shown in Fig. 8.8, 8.9 and 8.10 are somewhat disappointing, since they apparently do not manifest a significant improvement compared to the LDA results for SiC or the PBE results for Si and carbon C_{60} . All in all, the spectra exhibit a slight blue shift, whereas peak intensities do not change qualitatively. This result is not too surprising. As already discussed in Ref. [128] the TPSS functional possesses only a negligible $1/q^2$ divergence

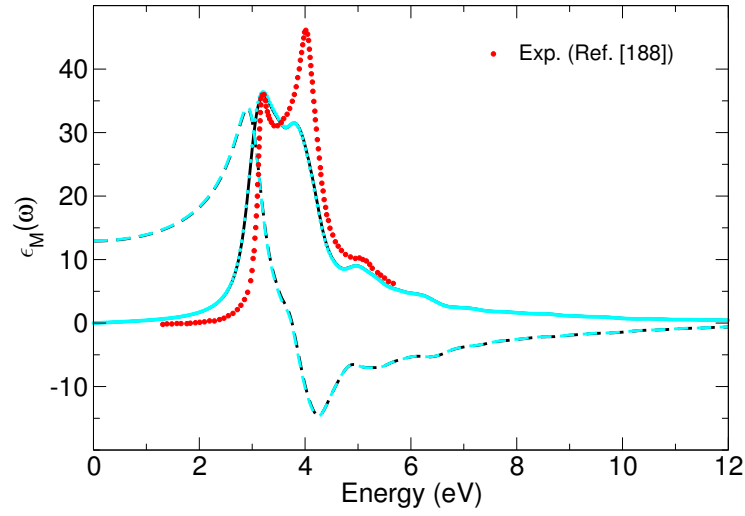


Figure 8.6.: Real (broken) and imaginary (full and dotted) part of the macroscopic dielectric function $\epsilon_M(\omega)$ of silicon (Si) calculated on a shifted $8 \times 8 \times 8$ $\mathbf{k}$ -point grid. The hybrid functional PBEh is used to approximate exchange and correlation effects. Color coding as in Fig. 8.2. Experimental data (red dots) are taken from Ref. [188] and are additionally red-shifted by 0.23 eV.

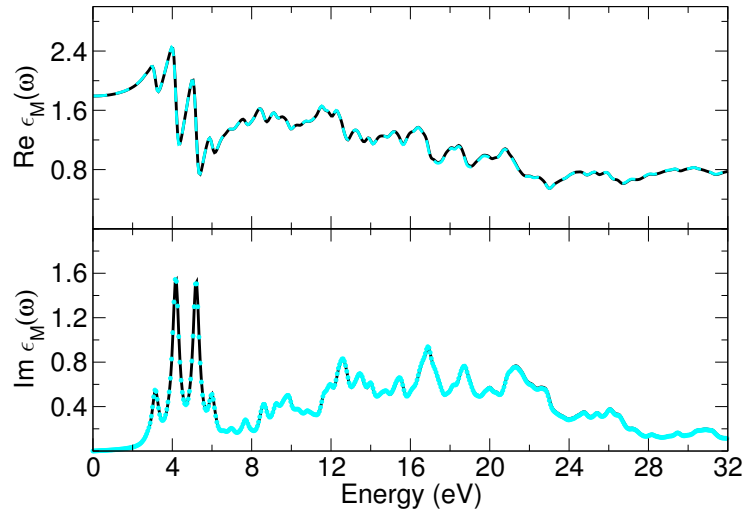


Figure 8.7.: Real and imaginary part of the macroscopic dielectric function $\epsilon_M(\omega)$ of carbon C_{60} . The PBEh hybrid functional is applied. Color coding as in Fig. 8.2.

for the exchange correlation kernel. This explains why the spectra are hardly modified compared to standard local or semi-local functionals. Furthermore, in the present implementation we have even neglected the $1/q^2$ divergence of the kernel as discussed at the end of section 8.1. This approximation is fully justified for the TPSS functional, as shown in Ref. [128].

Other functionals, for instance the VS98 functional,[128] yield better agreement with experiment (see Fig. 8.9), although it should be noted that the calculations in Ref. [128] only included a long wave length approximation to the exact exchange correlation kernel. Our present code in principle allows to include the response at all wave vectors, once the diverging part is properly taken into account [compare Eq. (8.18)].

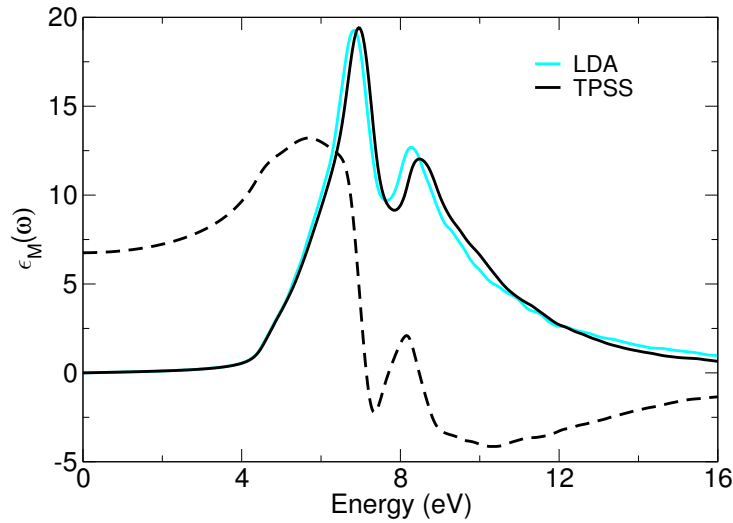


Figure 8.8.: Real (black broken) and imaginary (black) part of the macroscopic dielectric function $\epsilon_M(\omega)$ of silicon carbide (SiC). Calculations were performed using the meta-GGA functional (TPSS) on a shifted $24 \times 24 \times 24$ $\mathbf{k}$ -point grid. In cyan color, the imaginary part of $\epsilon_M(\omega)$ from Fig. 8.2 is shown. Results are obtained from the time evolution method.

8.4. Summary and conclusion

In this article, we have addressed the calculation of the macroscopic dielectric function from two equivalent methods. On the one hand, the Casida method is the common approach to calculate the linear response of the density matrix and, concomitantly, the polarizability. Within the long wave length limit, it allows then to obtain the macroscopic dielectric function. The disadvantage of the Casida approach is that it requires to store a huge matrix. The rank of this matrix is determined by the number of occupied times the number of considered unoccupied orbitals times the number of $\mathbf{k}$ -points. The other common approach is time evolution. After application of a long wave length delta pulse in time, the time evolution of the induced dipole moments allows one to calculate the macroscopic polarizability from the time evolution of the orbitals. Our present implementation uses a very simple second order difference method. To

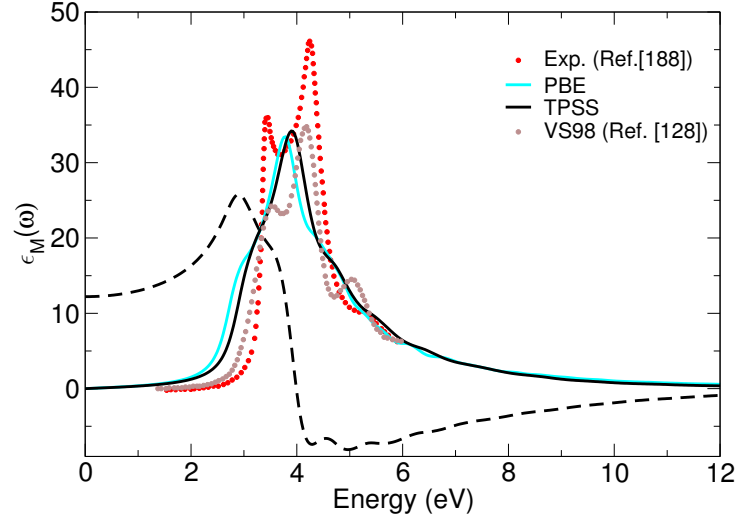


Figure 8.9.: Macroscopic dielectric function of silicon (Si). Color coding, $\mathbf{k}$ -point grid and method as in Fig. 8.8. In cyan color, the imaginary part of $\epsilon_M(\omega)$ from Fig. 8.3 is shown. Results for the imaginary part of ϵ_M obtained with the meta-GGA functional VS98 (brown dots) are taken from Ref. [128]. Experimental data (red dots) are obtained from Ref. [188].

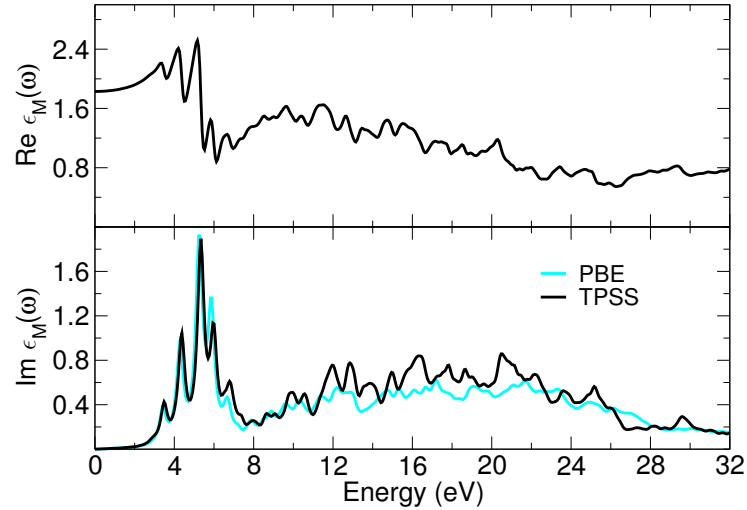


Figure 8.10.: Macroscopic dielectric function $\epsilon_M(\omega)$ of carbon C_{60} . Color coding and method as in Fig. 8.8. In cyan color, the imaginary part of $\epsilon_M(\omega)$ from Fig. 8.4 is shown.

preserve orthogonality of the propagated orbitals at every time step, we project them onto a set of orthogonal virtual orbitals. This facilitates a simple implementation for generalized eigenvalue problems (PAW method) and improves the stability allowing for large time steps compared to other time evolution implementations that only propagate the orbitals in time. Therefore, we can also use a fairly long simulation time which yields an accurate resolution of individual eigenmodes Ω . Furthermore, we have discussed how calculated frequencies are effected by the use of a second order difference scheme, and how the resulting error can be easily corrected using a simple relation [see Eq. (8.26)].

We have used both methods for standard DFT and hybrid functionals paying particular attention to the computational complexity of the two approaches. The presented results for the bulk systems silicon carbide and silicon, and for the molecule C_{60} clearly demonstrate the exact equivalence of the Casida method and the time evolution method as they produce virtually indistinguishable spectra. With regard to the computational complexity, the time evolution method benefits from its approximately linear scaling w.r.t. the number of considered occupied bands and $\mathbf{k}$ -points and linear scaling w.r.t the number of plane wave coefficients. Hence, the computational complexity is comparable to an ordinary DFT ground state calculation. In fact, in our present implementation, we simply reused the ground state routines; the only difference is that the initial orbitals are prepared using a short delta 'kick' and then evolved in time. Compared to the Casida approach, time evolution also benefits from a reduced storage demand, since one has to store only the time developed transition coefficients. Those require at most the same amount of storage as the occupied orbitals in groundstate calculations. This allows to go beyond the $\mathbf{k}$ -point settings usually applied in the Casida method. In practice, we, however, found that time evolution is only competitive, if the xc-kernel is approximated by a (semi)-local approximation LDA, PBE or a meta-GGA functional. For such functionals, time evolution is on average more than 40 times faster than solving the eigenvalue problem in the Casida approach for typical $\mathbf{k}$ -point grids.

The drawback of the time evolution method is the repetitive update and application of the Hamiltonian at every time step. This makes the inclusion of nonlocal exchange very time consuming, since the evaluation of the exchange kernel scales quadratic, both with the number of $\mathbf{k}$ -points as well as with the number of occupied bands. As we know from groundstate calculations, evaluation of the nonlocal exchange can take up to 100-1000 times longer than calculation of the Hamiltonian for standard DFT calculations, if many $\mathbf{k}$ -points are included. Hence, the time evolution turns out to be not competitive with the diagonalization of the Casida equation for hybrid functionals: although we have used about 3 times less $\mathbf{k}$ -points than for the DFT calculations, the inclusion of exact exchange increases the computational effort by a factor 110 for silicon carbide and by a factor 60 for silicon. If only a single $\mathbf{k}$ -point is used, for instance, if the molecule C_{60} in a box is considered, the total computational time for time evolution is only about a factor 8 larger for hybrid functionals than for semi-local functionals. In this case, the time evolution can be competitive with diagonalization of the Casida equation, although in our specific test case, it was still slower than solving the Casida equation. Hence, for the systems considered here, solving the Casida equation for hybrid functionals is *always* superior to the time

evolution of the orbitals.

Another disadvantage of the time-evolution should also not remain unmentioned. The eigenfunctions of the excited problem are not readily available in TE, since TE only yields the density of states of the optically excited system. This makes a precise analysis of the orbitals involved in the excitations difficult, if not impossible.

The main drawback of solving the Casida equation, i.e. the huge memory requirements, has already been mentioned. What has yet not been pointed out is that implementing the Casida approach requires one to implement the second derivative of the exchange-correlation kernel. These are readily available only for few selected functionals. Here time evolution can have an advantage, and in fact, our present time evolution implementation works for any functional for which groundstate calculations are possible. This gave us the opportunity to evaluate optical properties for the meta-GGA functional TPSS. Unfortunately, we found no improvement compared to standard DFT functionals: the excitonic features, which are absent using local or semi-local approximations for the xc-kernel, are also absent using the meta-GGA functional TPSS. Compared to our semi-local DFT calculations, we find for all three considered systems only a slightly blue shifted spectrum, while the peak intensities remained nearly unchanged. We attribute this observation to the small contribution of the singularity correction from the TPSS xc-kernel as argued by the authors in Ref. [128].

In summary, time evolution and solving the Casida equation yield exactly identical spectra, and both approaches have advantages as well as disadvantages. Clearly for local, semi-local or meta-GGA functionals, time evolution methods are extremely efficient. For hybrid functionals, though, the Casida approach is faster, since it avoids the repetitive evaluation of the nonlocal exchange kernel.

9. Final summary

The present thesis aims to give a deeper insight of the calculation of the macroscopic dielectric function. This quantity is accessible by experimental investigations and yields the optical absorption spectrum for any kind of materials. It takes therefore an important role within the research of new materials that are potentially applicable in the field of photovoltaics.

In the first part of this thesis the theoretical background has been presented and paves the way to the final derivation of the dielectric function. Its numerical calculation, within an *ab-initio* approach, is usually performed in a three step-method that starts with a density-functional theory calculation to obtain the Kohn-Sham orbitals and corresponding eigenenergies. As this method suffers from yielding proper band structures in particular for semiconductors, many-body effects are usually taken into account, additionally. This is done in terms of the Green's function formalism. The underlying quantity to obtain the desired quasiparticle corrections, is the self-energy that is usually approximated within the G_0W_0 -approximation. In this work the computational even more elaborate self-consistent GW -approximation is exploited, where the Kohn-Sham energies but also the corresponding Kohn-Sham orbitals are updated iteratively. As this step is very expensive, the scissor-operator technique is very often applied which simply shifts the unoccupied Kohn-Sham eigenenergies to higher energies. However, this method yields a less improved bandstructure compared to the self-consistent GW approach. More importantly, the previously calculated one-electron orbitals and corresponding eigenenergies serve as input to calculate the desired dielectric function in the final third step. Therefore, the inclusion of quasiparticle effects is inevitable to have excellent agreement of results from *ab-initio* methods with experiment. As it has been demonstrated in section 3.5.3, the dielectric function is obtained from the density correlation function, while the latter one obeys a closed integral-equation, the Bethe-Salpeter equation (BSE). Its solution is the central problem and covers the first key point of this thesis. In the theory part, section 4.1.7, the formal solution of the Bethe-Salpeter equation is derived. As discussed in this section, a non-Hermitian eigenvalue problem needs to be solved to calculate the density correlation function. This can be avoided, if the commonly applied Tamm-Dancoff approximation (TDA) is exploited. It turns the underlying eigenvalue problem into an Hermitian one that can be solved numerically with standard eigenvalue solvers. One task of this thesis, was to introduce the method of time inversion symmetry that allows to calculate the full eigenvalue problem and thus to obtain the dielectric function beyond the Tamm-Dancoff approximation. This topic has been addressed in the first publication, presented in section 7. In there, we also give evidence why results for the optical absorption spectrum beyond the Tamm-Dancoff approximation have little difference compared to those obtained with the TDA and give furthermore reasons when this statement does not hold anymore. The second key point in this thesis considers the limitation of the Bethe-Salpeter approach. As the density correlation function

is represented within a basis set of two-orbital states (transition pairs), namely a product of one occupied and one unoccupied orbital, the resulting and aforementioned eigenvalue problem is numerically solvable only for matrix sizes of up to 100.000-150.000. Due to this, the number of transition pairs limits the solution of the Bethe-Salpeter equation. For this reason, we have implemented the time evolution of orbitals as described in the second publication, section 8. This method allows to calculate the polarizability from which the macroscopic dielectric function is obtained. Within the time dependent density functional theory, the TE method is equivalent with the Casida method, while the latter one involves an equivalent algebraic eigenvalue problem as the BSE method. Therefore, we can make statements about the computational efficiency of both methods. With the TE method in hand, the Casida matrix is not required at all, to calculate the polarizability and subsequently the macroscopic dielectric function. This has a huge computational advantage, in terms of memory requirements (there is no matrix to be stored) and compute time, since there is no eigenvalue problem to be solved numerically. Therefore, the limitation of the number of transition pairs is removed. This allows to calculate optical absorption spectra for systems that contains more than a few atoms per unit cell, as it is usually done within the Casida/BSE approach. In section 8 we also discuss the advantages of the TE method but also show its limitations and argue when the TE method becomes competitive.

In summary, I present the calculation of the dielectric function obtained from two different methods. On the one hand the BSE approach is the common method that yields reliable results for optical absorption spectra within the Tamm-Dancoff approximation. In this work, we give evidence for the success of the TDA on the one hand, but also show when this approximation fails. In order to go beyond the TDA, the time inversion symmetry has been exploited and allows to solve the full eigenvalue problem. As a second key point, the time evolution of orbitals has been introduced within the framework of time dependent density functional theory. Its computational advantages have been presented in terms of compute time and offers the possibility to calculate optical absorption spectra for nanostructures.

A. Functional derivative

Given a linear functional $F[f]$, its variation with respect to the argument f is defined as the limes

$$\lim_{\tau \rightarrow 0} \frac{F[f + \tau h] - F[f]}{\tau} = \left. \frac{d}{d\tau} F[f + \tau h] \right|_{\tau=0}. \quad (\text{A.1})$$

If the limes in A.1 exists, the functional F is said to be differentiable. Thereby, h is an arbitrary function with a given norm $\|h\|$. From functional analysis, the functional $F[f + \tau h]$ obeys the condition $F[f + \tau h] \rightarrow F[f]$ for $\|h\| \rightarrow 0$. As the test function h is arbitrary it may be chosen as a simple delta function, that eventually yields the definition of the functional derivative as the following:

$$\frac{\delta F}{\delta f(x')} := \lim_{\tau \rightarrow 0} \frac{F[f + \tau \delta(x - x')] - F[f]}{\tau} \quad (\text{A.2})$$

From Eq.(A.2) the variation of the functional, i.e. δF , is then obtained by

$$\delta F =: F[f + \delta f] - F[f] = \int dx' \frac{\delta F}{\delta f(x')} \delta f(x') \quad (\text{A.3})$$

with $\delta f(x') = \tau \delta(x - x')$.

Chain rule of functional derivative

Like in ordinary analysis, a chain rule can also be stated for the functional derivative. Let F be a functional of the form $F = F[G[f]]$, where G is a functional of f , the derivative w.r.t f is then given by

$$\frac{\delta F}{\delta f(x')} = \int dx \frac{\delta F[G]}{\delta G[f](x)} \frac{\delta G[f](x)}{\delta f(x')}. \quad (\text{A.4})$$

B. Second quantization - Coulomb interaction

In order to obtain the representation of the Coulomb interaction [Eq.(2.3)] within the framework of second quantization, one finds with Eq.(3.13):

$$\begin{aligned}
\hat{V}_{\text{int,sq}} &= \frac{1}{2} \int d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}_1 d\mathbf{r}_2 \hat{\psi}^\dagger(\mathbf{r}'_1) \hat{\psi}^\dagger(\mathbf{r}'_2) \langle \mathbf{r}'_1 \mathbf{r}'_2 | \frac{e^2}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} | \mathbf{r}_1 \mathbf{r}_2 \rangle \hat{\psi}(\mathbf{r}_2) \hat{\psi}(\mathbf{r}_1) \\
&= \frac{1}{2} \int d\mathbf{r}'_1 d\mathbf{r}'_2 d\mathbf{r}_1 d\mathbf{r}_2 \hat{\psi}^\dagger(\mathbf{r}'_1) \hat{\psi}^\dagger(\mathbf{r}'_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \underbrace{\langle \mathbf{r}'_1 \mathbf{r}'_2 | \mathbf{r}_1 \mathbf{r}_2 \rangle}_{\delta(\mathbf{r}'_1 - \mathbf{r}_1) \delta(\mathbf{r}'_2 - \mathbf{r}_2)} \hat{\psi}(\mathbf{r}_2) \hat{\psi}(\mathbf{r}_1) \\
&= \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \hat{\psi}^\dagger(\mathbf{r}_1) \hat{\psi}^\dagger(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \hat{\psi}(\mathbf{r}_2) \hat{\psi}(\mathbf{r}_1).
\end{aligned} \tag{B.1}$$

From Eq.(B.1) the expectation value of $\langle \Psi | \hat{V}_{\text{int,sq}} | \Psi \rangle$ with $|\Psi\rangle \in \mathcal{H}_1^+$ becomes zero as a consequence of the fundamental relation, that no particle can be removed from the vacuum state $|0\rangle$ ¹. The action of the field operators on the rhs then yields:

$$\begin{aligned}
\hat{\psi}(\mathbf{r}_2) \hat{\psi}(\mathbf{r}_1) | \Psi \rangle &= \hat{\psi}(\mathbf{r}_2) \hat{\psi}(\mathbf{r}_1) \hat{\psi}^\dagger(\mathbf{r}_1) | 0 \rangle \\
&= -\hat{\psi}(\mathbf{r}_1) \hat{\psi}(\mathbf{r}_2) \hat{\psi}^\dagger(\mathbf{r}_1) | 0 \rangle \\
&= \hat{\psi}(\mathbf{r}_1) \left[\hat{\psi}^\dagger(\mathbf{r}_1) \hat{\psi}(\mathbf{r}_2) - \delta(\mathbf{r}_1 - \mathbf{r}_2) \right] | 0 \rangle \\
&= 0.
\end{aligned} \tag{B.2}$$

¹ $\hat{\psi}(\mathbf{r}) | 0 \rangle = 0$

C. Fourier transform

The Fourier transform between the time and frequency domain used in this work employs the following conventions:

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega f(\omega) e^{-i\omega t} \longleftrightarrow f(\omega) = \int_{-\infty}^{+\infty} dt f(t) e^{i\omega t}. \quad (\text{C.1})$$

Fourier transform of the Theta function

In the context of the Green's function formalism, the theta function appears in the definition of the Green's function and ensures either the causal or retarded/advanced properties. To obtain the frequency component for G the following identity is exploited

$$\Theta(t_1 - t_2) = \lim_{\eta \rightarrow 0} \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega(t_1 - t_2)}}{\omega + i\eta}. \quad (\text{C.2})$$

Fourier transform with periodic boundary conditions

Based on the crystalline structure of a solid, one is faced with a resulting symmetry that every function has to obey. Thereby, the crystal consists of a smallest symmetric region, the unit cell, that contains all non-equivalent space points with respect to a given crystal symmetry. This cell is spanned by the corresponding basis vectors $\{\mathbf{a}_i\}$ with $i = 1, 2, 3$. In order to have a complete description of the solid, the unit cell is enriched with a given basis set of atoms and is then continued periodically along the Bravais vectors $\mathbf{R}$ given by

$$\mathbf{R} = \sum_{i=1}^3 n_i \mathbf{a}_i. \quad (\text{C.3})$$

For finite extended crystalline structures with a volume V , the Born and von Karman boundary conditions [227] need to be satisfied. Therefore, the Fourier transform of a spatially function $f(\mathbf{r})$ can be expressed by a series of plane waves with momentum vector $\mathbf{k} + \mathbf{G}$

$$f(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}, \mathbf{G}} f(\mathbf{k} + \mathbf{G}) e^{i(\mathbf{k} + \mathbf{G})\mathbf{r}}. \quad (\text{C.4})$$

Hereby, the set of reciprocal lattice vectors $\{\mathbf{G}\}$ constitutes the reciprocal space to the real space lattice associated with the set of Bravais lattice vectors $\{\mathbf{R}\}$. They obey the condition

$$\{\mathbf{R}\mathbf{G}\} = 2\pi m \quad \text{with} \quad m \in \mathbb{Z}. \quad (\text{C.5})$$

The vector $\mathbf{k}$ in Eq.(C.4) belongs to the first Brillouin zone, the reciprocal counterpart of the real space unit cell. It hence contains all non-equivalent smallest reciprocal lattice vectors. Their number depends on the entire periodic region V and is discrete, as long as the crystal volume is finite. On the contrary, the set of $\mathbf{G}$ -vectors is infinitely large as it describes the periodicity of the unit cell. Their number is artificially truncated within a numerical calculation. To finally obtain the Fourier component, the inverse Fourier transformation yields

$$f(\mathbf{k} + \mathbf{G}) = \int d\mathbf{r} e^{-i(\mathbf{k} + \mathbf{G})\mathbf{r}} f(\mathbf{r}). \quad (\text{C.6})$$

If a two point function $f(\mathbf{r}', \mathbf{r}')$ is considered, such as the dielectric function $\epsilon(\mathbf{r}, \mathbf{r}')$, the Fourier expansion becomes

$$f(\mathbf{r}, \mathbf{r}') = \frac{1}{V} \sum_{\mathbf{k}, \mathbf{G}} \sum_{\mathbf{k}', \mathbf{G}'} e^{i(\mathbf{k} + \mathbf{G})\mathbf{r}} f(\mathbf{k} + \mathbf{G}, \mathbf{k}' + \mathbf{G}') e^{-i(\mathbf{k}' + \mathbf{G}')\mathbf{r}'}, \quad (\text{C.7})$$

with the Fourier coefficient

$$f(\mathbf{k} + \mathbf{G}, \mathbf{k}' + \mathbf{G}') = \frac{1}{V} \iint d\mathbf{r} d\mathbf{r}' e^{-i(\mathbf{k} + \mathbf{G})\mathbf{r}} f(\mathbf{r}, \mathbf{r}') e^{i(\mathbf{k}' + \mathbf{G}')\mathbf{r}'}. \quad (\text{C.8})$$

If, however, the function $f(\mathbf{r}, \mathbf{r}')$ obeys the periodicity of the crystal lattice structure, i.e. $f(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}) = f(\mathbf{r}, \mathbf{r}')$, the Fourier coefficient $f(\mathbf{k} + \mathbf{G})$ is solely described by the reciprocal lattice vector, i.e. $f(\mathbf{k} + \mathbf{G}) = \delta_{\mathbf{k},0} f(\mathbf{G})$. For the corresponding coefficient of the two point function one obtains [51]

$$\begin{aligned} f(\mathbf{k} + \mathbf{G}, \mathbf{k}' + \mathbf{G}') &= \int d\mathbf{r} d\mathbf{r}' e^{-i(\mathbf{k} + \mathbf{G})\mathbf{r}} f(\mathbf{r}, \mathbf{r}') e^{i(\mathbf{k}' + \mathbf{G}')\mathbf{r}'} \\ &= \iint d\mathbf{r} d\mathbf{r}' e^{-i(\mathbf{k} + \mathbf{G})\mathbf{r}} f(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}) e^{i(\mathbf{k}' + \mathbf{G}')\mathbf{r}'} \\ &= \iint d\mathbf{r} d\mathbf{r}' e^{-i(\mathbf{k} + \mathbf{G})(\mathbf{r} - \mathbf{R})} f(\mathbf{r}, \mathbf{r}') e^{i(\mathbf{k}' + \mathbf{G}')(\mathbf{r}' - \mathbf{R})} \\ &= e^{i(\mathbf{k} - \mathbf{k}')\mathbf{R}} e^{i(\mathbf{G} - \mathbf{G}')\mathbf{R}} \iint d\mathbf{r} d\mathbf{r}' e^{-i(\mathbf{k} + \mathbf{G})\mathbf{r}} f(\mathbf{r}, \mathbf{r}') e^{i(\mathbf{k}' + \mathbf{G}')\mathbf{r}'} \end{aligned} \quad (\text{C.9})$$

Equation (C.9) is valid only if the difference vector $\mathbf{k} - \mathbf{k}'$ is a reciprocal lattice vector such that $\mathbf{k} = \mathbf{k}' + \tilde{\mathbf{G}}$. But this implies the vector $\mathbf{k}$ to be symmetrically equivalent to $\mathbf{k}'$ and thus would lie outside the first Brillouin zone and reveals the contradiction that both vectors $\mathbf{k}$ and $\mathbf{k}'$ belong to the first BZ. Hence it is the reciprocal vector $\tilde{\mathbf{G}} = 0$ that eventually fulfills the necessary condition $e^{i(\mathbf{k} - \mathbf{k}')\mathbf{R}} = 1$. In turn the Fourier coefficient is diagonal with respect to the $\mathbf{k}$ component:

$$f(\mathbf{k} + \mathbf{G}, \mathbf{k}' + \mathbf{G}') = \delta_{\mathbf{k}, \mathbf{k}'} f(\mathbf{k} + \mathbf{G}, \mathbf{k}' + \mathbf{G}'). \quad (\text{C.10})$$

By Eq.(C.9) one easily verifies, why the Fourier coefficient $f(\mathbf{k} + \mathbf{G})$ depends only on the single reciprocal lattice vector $\mathbf{G}$.

D. Pictures in quantum mechanics

Schrödinger picture

The time dependent Schrödinger equation describes the dynamics of a quantum mechanical state

$$i\hbar \frac{d}{dt} |\Psi(t)\rangle_S = \hat{H}_S |\Psi(t)\rangle_S. \quad (\text{D.1})$$

It is based on the assumption of a conservative system whose energy is given by the Hamiltonian, such that the eigenstates oscillates with their corresponding eigenenergy. The time evolution of an arbitrary state $|\Psi(t)\rangle_S$ is formally governed by a time evolution operator $\hat{U}(t_1, t_0)$. Therefore, the time dependent Schrödinger equation can be rewritten as

$$i\hbar \frac{d}{dt} \hat{U}(t, t_0) |\Psi(t_0)\rangle_S = \hat{H}_S \hat{U}(t, t_0) |\Psi(t_0)\rangle_S. \quad (\text{D.2})$$

Since Eq.(D.2) shall be valid for every eigenstates of the Hamiltonian, the time evolution operator is then obtained from the solution

$$i\hbar \frac{d}{dt} \hat{U}(t, t_0) = \hat{H}_S \hat{U}(t, t_0), \quad (\text{D.3})$$

which in the case of an time independent Hamiltonian (conservative system) takes the usual expression

$$\hat{U}(t_1, t_0) = e^{-\frac{i}{\hbar} \hat{H}_S(t_1 - t_0)} \equiv \hat{U}_0(t_1, t_0), \quad (\text{D.4})$$

with the initial condition $\hat{U}(t_0, t_0) = \mathbb{1}$. However, the formal solution of Eq.(D.3), i.e.

$$\hat{U}(t_1, t_0) = \mathbb{1} + \frac{1}{i\hbar} \int_{t_0}^{t_1} dt'_1 \hat{H}_S(t'_1) \hat{U}(t'_1, t_0), \quad (\text{D.5})$$

allows likewise to solve for the time evolution operator if the Hamiltonian is time dependent. The solution to Eq.(D.5) is then obtained by iteration starting with the initial condition for $\hat{U}$:

$$\begin{aligned} \hat{U}(t_1, t_0) &= \mathbb{1} + \frac{1}{i\hbar} \int_{t_0}^{t_1} dt'_1 \hat{H}_S(t'_1) \left[\mathbb{1} + \frac{1}{i\hbar} \int_{t_0}^{t'_1} dt'_2 \hat{H}_S(t'_2) \hat{U}(t'_2, t_0) \right] + \dots \\ &= \mathbb{1} + \frac{1}{i\hbar} \int_{t_0}^{t_1} dt'_1 \hat{H}_S(t'_1) + \frac{1}{(i\hbar)^2} \int_{t_0}^{t_1} dt'_1 \hat{H}_S(t'_1) \int_{t_0}^{t'_1} dt'_2 \hat{H}_S(t'_2) \hat{U}(t'_2, t_0) + \dots \\ &= \mathbb{1} + \hat{U}^{(1)}(t, t_0) + \hat{U}^{(2)}(t, t_0) + \dots \end{aligned} \quad (\text{D.6})$$

Since the time evolution operator itself is unknown, but appears in the series expansion, it makes the solution of $\hat{U}$ rather difficult. However, if the stationary Hamiltonian $\hat{H}_S$ is given and hence the solution for $\hat{U}_0$ is known, it is convenient to exploit a product ansatz for the full time evolution operator, such as [228]

$$\hat{U}(t_1, t_0) = \hat{U}_0(t_1, t_0) \hat{U}_I(t_1, t_0) \quad (\text{D.7})$$

This allows to evaluate the differential equation for the time evolution operator Eq.(D.3) as shown below:

$$i\hbar \left[\frac{d}{dt} U(t, t_0) \right] U'(t, t_0) + i\hbar U(t, t_0) \left[\frac{d}{dt} U'(t, t_0) \right] = H_S(t) U(t, t_0) U'(t, t_0) \quad (\text{D.8})$$

After multiplication with $\hat{U}_0^\dagger$ from the lhs one obtains:

$$\begin{aligned} i\hbar \frac{d}{dt} \hat{U}_I(t, t_0) &= U_0^\dagger(t, t_0) \hat{H}_S(t) \hat{U}_0(t, t_0) \hat{U}_I(t, t_0) - i\hbar \left[\frac{d}{dt} \hat{U}_0(t, t_0) \right] U_I(t, t_0) \\ &= \hat{U}_0^\dagger(t, t_0) \left[\hat{H}_S(t) \hat{U}_0(t, t_0) - i\hbar \frac{d}{dt} \hat{U}_0(t, t_0) \right] U_I(t, t_0) \\ &= \hat{U}_0^\dagger(t, t_0) \left[\hat{H}_S(t) \hat{U}_0(t, t_0) - \hat{H}_S \hat{U}_0(t, t_0) \right] \hat{U}_I(t, t_0) \\ &= \hat{U}_0^\dagger(t, t_0) \left\{ \left[\hat{H}_S(t) - \hat{H}_S \right] \hat{U}_0(t, t_0) \right\} \hat{U}_I(t, t_0) \\ &= \left[\hat{U}_0^\dagger(t, t_0) \hat{H}_S'(t) \hat{U}_0(t, t_0) \right] \hat{U}_I(t, t_0) \\ &= \hat{H}_I'(t) \hat{U}_I(t, t_0) \end{aligned} \quad (\text{D.9})$$

From the last two lines we can draw the conclusion that any time-dependent Hamiltonian $\hat{H}_S(t)$ can be separated into a time-independent part $\hat{H}_S$ plus a time-dependent part $\hat{H}_S'(t)$. As, in general, the solution of the time-independent problem is known and hence the corresponding time evolution operator $\hat{U}_0$, we can decouple the full time evolution governed by $\hat{H}_S(t)$ into the transformed time evolution, which is now driven by the time-dependent part $\hat{H}_I'(t)$ only.

Interaction picture

The transition from the Schrödinger picture to the interaction picture is, as one deduces from Eq.(D.9), ruled by the unitary operator $\hat{U}_0^\dagger$. For an arbitrary operator $\hat{O}_S(t)$ within the Schrödinger picture, the corresponding operator in the Dirac picture is then given by

$$\hat{O}_D(t) = e^{\frac{i}{\hbar} \hat{H}_S t} \hat{O}_S e^{-\frac{i}{\hbar} \hat{H}_S t}. \quad (\text{D.10})$$

By considering the time derivative of Eq.(D.10), one may write down the corresponding equation of motion of $\hat{O}_D(t)$ as the following

$$i\hbar \frac{\partial}{\partial t} \hat{O}_I(t) = \left[\hat{O}_I(t), \hat{H}_S \right] + i\hbar \frac{\partial \hat{O}_I(t)}{\partial t} \quad (\text{D.11})$$

Furthermore, the time dependent state vector (in the interaction picture) is then defined as

$$|\Psi(t)\rangle_I = e^{\frac{i}{\hbar}\hat{H}_S t} |\Psi(t)\rangle_S, \quad (\text{D.12})$$

while its time evolution is carried by $\hat{U}_I$, i.e.

$$|\Psi(t)\rangle_I = \hat{U}_I(t, t_0) |\Psi(t_0)\rangle_I. \quad (\text{D.13})$$

The equation of motion for $\hat{U}_I$ is already given in Eq.(D.9) and allows to write down its formal solution:

$$\hat{U}_I(t_1, t_0) = \mathbb{1} + \frac{1}{i\hbar} \int_{t_0}^{t_1} dt'_1 \hat{H}'_I(t'_1) \hat{U}_I(t'_1, t_0) \quad (\text{D.14})$$

Again, we can proceed as in Eq.(D.6) and solve $\hat{U}_I(t_1, t_0)$ iteratively. If one restricts the iteration up to first order, one obtains

$$\hat{U}_I(t_1, t_0) = \mathbb{1} + \frac{1}{i\hbar} \int_{t_0}^{t_1} dt'_1 \hat{H}'_I(t'_1) + \dots \quad (\text{D.15})$$

With the solution of the time evolution operator within the interaction picture, we also obtain the corresponding equation within the Schrödinger picture, which w.r.t Eq.(D.7) reads

$$\hat{U}(t_1, t_0) = \hat{U}_0(t_1, t_0) + \frac{1}{i\hbar} \int_{t_0}^{t_1} dt'_1 \hat{U}_0(t_1, t'_1) \hat{H}'_S(t'_1) \hat{U}_0(t'_1, t_0) + \dots \quad (\text{D.16})$$

In fact, both equations, Eq.(D.15) and Eq.(D.16) are equivalent in their corresponding quantum mechanical picture and describe the time evolution of a quantum state under the influence of a small perturbation that is given by $\hat{H}'_{S,I}$.

Heisenberg picture

The transition into the Heisenberg picture allows to transfer the dynamics of a quantum mechanical state to the operators. With the unitary transformation

$$|\Psi(t)\rangle_H = \hat{U}^\dagger(t_1, t_0) |\Psi(t)\rangle_S = \hat{U}(t_0, t_1) |\Psi(t)\rangle_S = |\Psi(t_0)\rangle_S = |\Psi\rangle_H, \quad (\text{D.17})$$

all state vectors in the Heisenberg picture become time independent. In contrast to it, any operator is transformed like

$$\hat{O}_H(t) = \hat{U}^\dagger(t_1, t_0) \hat{O}_S(t) \hat{U}(t_1, t_0) \quad (\text{D.18})$$

and obeys the equation of motion

$$i\hbar \frac{\partial}{\partial t} \hat{O}_H(t) = [\hat{O}_H(t), \hat{H}_H(t)] + i\hbar \frac{\partial \hat{O}_H(t)}{\partial t}. \quad (\text{D.19})$$

E. Thermodynamic Green's function formalism*

In order to augment the discussion about the Green's functions, their spectral properties shall be highlighted in this section by giving explicit expressions and showing their relation to the previous introduced formula in section 3.3.

Fourier transform

We begin with the explicit representation of the previously defined electron propagator [Eq.(3.17)] and insert a complete set of Heisenberg states $\{|\Psi_\alpha\rangle\}$, which yields

$$\begin{aligned} G^>(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \frac{1}{i\hbar} \sum_{\alpha, \alpha'} \varrho_\alpha \langle \Psi_\alpha | \hat{\psi}(\mathbf{r}_1 t_1) | \Psi_{\alpha'} \rangle \langle \Psi_{\alpha'} | \hat{\psi}^\dagger(\mathbf{r}_2 t_2) | \Psi_\alpha \rangle \\ &= \frac{1}{i\hbar} \sum_{\alpha, \alpha'} \varrho_\alpha \langle \Psi_\alpha | e^{\frac{i}{\hbar} \hat{H} t_1} \hat{\psi}(\mathbf{r}_1) e^{-\frac{i}{\hbar} \hat{H} t_1} | \Psi_{\alpha'} \rangle \langle \Psi_{\alpha'} | e^{\frac{i}{\hbar} \hat{H} t_2} \hat{\psi}^\dagger(\mathbf{r}_2) e^{-\frac{i}{\hbar} \hat{H} t_2} | \Psi_\alpha \rangle \\ &= \frac{1}{i\hbar} \sum_{\alpha, \alpha'} \varrho_\alpha \langle \Psi_\alpha | \hat{\psi}(\mathbf{r}_1) | \Psi_{\alpha'} \rangle \langle \Psi_{\alpha'} | \hat{\psi}^\dagger(\mathbf{r}_2) | \Psi_\alpha \rangle e^{-\frac{i}{\hbar} (t_1 - t_2) (\varepsilon_{\alpha'} - \varepsilon_\alpha)}. \end{aligned} \quad (\text{E.1})$$

Under the assumption of a time independent Hamiltonian $\hat{H}$, the electron propagator depends on the time differences $(t_1 - t_2)$ only. The field operators in the last line of Eq.(E.1) are given within the Schrödinger picture at time $t = 0$ and their matrix elements become non-zero if the eigenvalues N_α of the particle operator $\hat{N}$ differ by one, i.e. $N_{\alpha'} - N_\alpha = 1$. Similarly, the hole propagator [Eq.(3.18)] becomes

$$G^<(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) = -\frac{1}{i\hbar} \sum_{\alpha, \alpha'} \varrho_\alpha \langle \Psi_\alpha | \hat{\psi}^\dagger(\mathbf{r}_2) | \Psi_{\alpha'} \rangle \langle \Psi_{\alpha'} | \hat{\psi}(\mathbf{r}_1) | \Psi_\alpha \rangle e^{\frac{i}{\hbar} (t_1 - t_2) (\varepsilon_{\alpha'} - \varepsilon_\alpha)}, \quad (\text{E.2})$$

with the condition that $N_{\alpha'} - N_\alpha = -1$. Since both propagators are homogenous in the time difference $t_1 - t_2$, their Fourier transform in the frequency domain is then obtained with aid of Eq.(C.1) and yields

$$G^>(\mathbf{r}_1, \mathbf{r}_2; \omega) = -2i\pi \sum_{\alpha, \alpha'} \varrho_\alpha \langle \Psi_\alpha | \hat{\psi}(\mathbf{r}_1) | \Psi_{\alpha'} \rangle \langle \Psi_{\alpha'} | \hat{\psi}^\dagger(\mathbf{r}_2) | \Psi_\alpha \rangle \delta(\hbar\omega + \varepsilon_\alpha - \varepsilon_{\alpha'}) \quad (\text{E.3})$$

and

$$G^<(\mathbf{r}_1, \mathbf{r}_2; \omega) = 2i\pi \sum_{\alpha, \alpha'} \varrho_\alpha \langle \Psi_\alpha | \hat{\psi}^\dagger(\mathbf{r}_2) | \Psi_{\alpha'} \rangle \langle \Psi_{\alpha'} | \hat{\psi}(\mathbf{r}_1) | \Psi_\alpha \rangle \delta(\hbar\omega - \varepsilon_\alpha + \varepsilon_{\alpha'}). \quad (\text{E.4})$$

*The Refs. [60, 44, 49] have been used.

From Eq.(E.3) and Eq.(E.4) one reads off the exact excitation energies, i.e. $\pm(\varepsilon_\alpha + \varepsilon_{\alpha'})$ of the considered many-particle system. These energies can be additionally related to the chemical potential μ from Eq.(3.24) and shall be demonstrated here for the electron propagator¹:

$$\begin{aligned}\hbar\omega + \varepsilon_\alpha - \varepsilon_{\alpha'} &= \hbar\omega - \left[\varepsilon_{\alpha'}^{(N+1)} - \varepsilon_\alpha^N \right] \\ &= \hbar\omega - \left[\varepsilon_{\alpha'}^{(N+1)} - \varepsilon_\alpha^{(N+1)} \right] - \left[\varepsilon_\alpha^{(N+1)} - \varepsilon_\alpha^N \right] \\ &= \hbar\omega - \varepsilon^{(N+1)} - \mu.\end{aligned}\tag{E.5}$$

The chemical potential μ , defined as $(\frac{\partial E}{\partial N})_{SV}$ ², may be approximated by the energy difference $\varepsilon_\alpha^{(N+1)} - \varepsilon_\alpha^N$, if the difference of the particle number $(N+1) - N \ll N$, which is the case for a regular many-particle system containing about 10^{23} particles. Thus, the Lehman representation given by Eq.(3.23) reads in the zero-temperature limit as the following

$$\begin{aligned}G(\mathbf{r}_1, \mathbf{r}_2; \omega) &= \lim_{\eta \rightarrow 0^+} \sum_\alpha \left\{ \frac{\langle \Psi_0 | \hat{\psi}(\mathbf{r}_1) | \Psi_\alpha \rangle \langle \Psi_\alpha | \hat{\psi}^\dagger(\mathbf{r}_2) | \Psi_0 \rangle}{\hbar\omega - \varepsilon^{(N+1)} - \mu + i\hbar\eta} \right. \\ &\quad \left. + \frac{\langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{r}_2) | \Psi_\alpha \rangle \langle \Psi_\alpha | \hat{\psi}(\mathbf{r}_1) | \Psi_0 \rangle}{\hbar\omega + \varepsilon^{(N-1)} - \mu - i\hbar\eta} \right\}.\end{aligned}\tag{E.6}$$

From the representation above one notices that if $G(\omega)$ is continued into the complex frequency plane, it possesses poles slightly above and slightly below the real frequency axis. It is hence not analytic neither in the upper nor in the lower half complex plane. An extension of Eq.(E.6) for finite temperatures can be found in many text books, e.g. in Ref.[57].

Spectral representation at finite temperatures (real time arguments)

First of all, the Martin-Schwinger relation [Eq.(3.27)] allows to link the Fourier components of the electron and the hole propagator through the relation

$$G^<(\mathbf{r}_1, \mathbf{r}_2; \omega) = -e^{-\beta(\hbar\omega - \mu)} G^>(\mathbf{r}_1, \mathbf{r}_2; \omega),\tag{E.7}$$

and further relates both propagator functions to the spectral function [Eq.(3.25)]

$$G^<(\mathbf{r}_1, \mathbf{r}_2; \omega) = if(\hbar\omega) A(\mathbf{r}_1, \mathbf{r}_2, \omega)\tag{E.8}$$

$$G^>(\mathbf{r}_1, \mathbf{r}_2; \omega) = -i[1 - f(\hbar\omega)] A(\mathbf{r}_1, \mathbf{r}_2, \omega),\tag{E.9}$$

whereas $f(\hbar\omega)$ denotes the Fermi function

$$f(\hbar\omega) = \frac{1}{1 + e^{\beta(\hbar\omega - \mu)}}.\tag{E.10}$$

¹The corresponding expression for the hole propagator yields $\hbar\omega - \varepsilon_\alpha + \varepsilon_{\alpha'} = \hbar\omega + \varepsilon^{(N-1)} - \mu$, whereas $\varepsilon^{(N-1)}$ denotes the excitation energy if a particle is removed from the system, i.e. $\varepsilon^{(N-1)} \leq 0$.

²If Ψ_α denotes the ground state, the entropy S vanishes and the derivative is taken at constant volume only.

On the other hand, the definition of the causal Green's function at real time arguments [Eq.(3.22)] can be Fourier transformed with the aid of the Fourier transform of the theta function $\Theta(t_1 - t_2)$. The resulting Lehmann representation [Eq.(3.23)] is then obtained and can be further rewritten by use of the Dirac identity

$$\lim_{\eta \rightarrow 0} \frac{1}{\omega \pm i\eta} = \frac{\mathcal{P}}{\omega} \mp i\pi\delta(\omega) \quad (\text{E.11})$$

in the following way

$$G(\omega) = \lim_{\eta \rightarrow 0} \frac{i}{2\pi} \int_{-\infty}^{+\infty} d\omega' \left\{ \mathcal{P} \frac{G^>(\omega') + G^<(\omega')}{\omega - \omega'} - i\pi\delta(\omega - \omega') [G^>(\omega') + G^<(\omega')] \right\} \quad (\text{E.12})$$

where $\mathcal{P}$ denotes the principle value. Concerning the difference term of the rhs of Eq.(E.12), one finds with the use of Eq.(E.9) and Eq.(E.8)

$$\begin{aligned} G^>(\omega) + G^<(\omega) &= i[-1 + 2f(\hbar\omega)] \\ &= i \left[\frac{1 - e^{\beta(\hbar\omega - \mu)}}{1 + e^{\beta(\hbar\omega - \mu)}} \right] \\ &= i \left[\frac{e^{-\beta(\hbar\omega - \mu)/2} - e^{\beta(\hbar\omega - \mu)/2}}{e^{-\beta(\hbar\omega - \mu)/2} + e^{\beta(\hbar\omega - \mu)/2}} \right] \\ &= -i \tanh \left[\frac{\beta}{2}(\hbar\omega - \mu) \right] \end{aligned} \quad (\text{E.13})$$

that proofs the spectral representation of the causal Green's function as given by Eq.(3.26).

Retarded and advanced Green's function (real time arguments)

The retarded and advanced Green's function are defined as the following

$$\begin{aligned} G^{\text{ret}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \Theta(t_1 - t_2) \frac{1}{i\hbar} \left\langle \left[\psi(\mathbf{r}_1 t_1), \psi^\dagger(\mathbf{r}_2, t_2) \right]_+ \right\rangle \\ &= \Theta(t_1 - t_2) [G^>(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) - G^<(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2)] \end{aligned} \quad (\text{E.14})$$

$$\begin{aligned} G^{\text{adv}}(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \Theta(t_2 - t_1) \frac{1}{i\hbar} \left\langle \left[\psi(\mathbf{r}_1, t_1), \psi^\dagger(\mathbf{r}_2, t_2) \right]_+ \right\rangle \\ &= \Theta(t_2 - t_1) [G^>(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) - G^<(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2)] \end{aligned} \quad (\text{E.15})$$

and differ by the theta function as compared to the causal Green's function [Eq.(3.22)]. Both functions have a Lehmann representation similar to Eq.(3.23) but with a different but unchanged complex factor $+i\eta$ for the retarded and $-i\eta$ for the advanced Green's function in the denominators with respect to Eq.(3.23). With the aid of the Fourier transform of the theta function and the definition of the spectral function [Eq.(3.25)], one obtains the spectral representation of

the retarded and advanced Green's function, which is

$$G^{\text{ret/adv}}(\mathbf{r}_1, \mathbf{r}_2; \omega) = \lim_{\eta \rightarrow 0} \int_{-\infty}^{+\infty} d\omega' \frac{A(\mathbf{r}_1, \mathbf{r}_2; \omega')}{\omega - \omega' \pm i\eta}. \quad (\text{E.16})$$

In contrast to the causal Green's function, which possesses a spectral representation such as Eq.(E.16) only for the zero-temperature limit [see Eq.(3.24)], the expression above is valid for any finite temperatures. Furthermore, one reads off from Eq.(E.16) that the retarded and advanced Green's function are analytic in the upper and lower half complex frequency plane, respectively. The comparison of Eq.(3.24) and Eq.(E.16) immediately shows that if $G(\omega)$ is analytical continued to the complex plane, it resolves into the retarded Green's function by

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega + i\eta) \Big|_{T=0} = G^{\text{ret}}(\mathbf{r}_1, \mathbf{r}_2; \omega) \quad (\text{E.17})$$

and into the advanced Green's function

$$G(\mathbf{r}_1, \mathbf{r}_2; \omega - i\eta) \Big|_{T=0} = G^{\text{adv}}(\mathbf{r}_1, \mathbf{r}_2; \omega), \quad (\text{E.18})$$

respectively.

Properties of the spectral function

The spectral function turns out to be the central quantity as it gives the access to (i) excitation energies of the many-body system and (ii) generates all wanted Green's functions. Moreover, it retains the discontinuity of the causal Green's function as it can be also obtained by the difference of the retarded and advanced Green's function, i.e.

$$A(\mathbf{r}_1, \mathbf{r}_2; \omega) = i \left[G^{\text{ret}}(\mathbf{r}_1, \mathbf{r}_2; \omega) - G^{\text{adv}}(\mathbf{r}_1, \mathbf{r}_2; \omega) \right]. \quad (\text{E.19})$$

The proof of Eq.(E.19) exhibits the Dirac identity plus the definition of the spectral function Eq.(3.25). Furthermore, the spectral function is Hermitian

$$A(\mathbf{r}_1, \mathbf{r}_2; \omega) = A^*(\mathbf{r}_2, \mathbf{r}_1; \omega) \quad (\text{E.20})$$

and fulfills the important sum rule

$$\begin{aligned} \frac{1}{2\pi} \int d\omega A(\mathbf{r}_1, \mathbf{r}_2; \omega) &= \sum_{\alpha, \alpha'} \varrho_{\alpha} \left\{ \langle \Psi_{\alpha} | \psi(\mathbf{r}_1) | \Psi_{\alpha'} \rangle \langle \Psi_{\alpha'} | \psi^{\dagger}(\mathbf{r}_2) | \Psi_{\alpha} \rangle \right. \\ &\quad \left. + \langle \Psi_{\alpha} | \psi^{\dagger}(\mathbf{r}_2) | \Psi_{\alpha'} \rangle \langle \Psi_{\alpha'} | \psi(\mathbf{r}_1) | \Psi_{\alpha} \rangle \right\} \\ &= \langle \psi(\mathbf{r}_1) \psi^{\dagger}(\mathbf{r}_2) + \psi^{\dagger}(\mathbf{r}_2) \psi(\mathbf{r}_1) \rangle \\ &= \delta(\mathbf{r}_1 - \mathbf{r}_2). \end{aligned} \quad (\text{E.21})$$

Matsubara formalism

The treatment of the thermodynamic Green's function may be reduced to usage of complex time arguments only. This is due to the quasi-periodicity of the causal Green's function as a result of the Martin-Schwinger relation. The proof of this relation makes use of the cyclic property of the trace. From the expression of the electron propagator^{3,17} one finds with $\mathcal{Z} = \text{tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}\}$:

$$\begin{aligned}
 i\hbar G^>(\mathbf{r}_1 t_1, \mathbf{r}_2 t_2) &= \text{tr}\left\{e^{-\beta(\hat{H}-\mu\hat{N})}\hat{\psi}(\mathbf{r}_1 t_1)\hat{\psi}^\dagger(\mathbf{r}_2 t_2)\right\}\mathcal{Z}^{-1} \\
 &= \text{tr}\left\{\hat{\psi}^\dagger(\mathbf{r}_2 t_2)e^{-\beta\hat{H}}e^{\beta\mu\hat{N}}\hat{\psi}(\mathbf{r}_1 t_1)e^{\beta(\hat{H}-\mu\hat{N})}e^{-\beta(\hat{H}-\mu\hat{N})}\right\}\mathcal{Z}^{-1} \\
 &= \text{tr}\left\{\hat{\psi}^\dagger(\mathbf{r}_2 t_2)e^{-\beta\hat{H}}\hat{\psi}(\mathbf{r}_1 t_1)e^{\beta\hat{H}}e^{-\beta\mu}e^{-\beta(\hat{H}-\mu\hat{N})}\right\}\mathcal{Z}^{-1} \\
 &= e^{-\beta\mu}\left\langle\hat{\psi}^\dagger(\mathbf{r}_2 t_2)\hat{\psi}(\mathbf{r}_1 t_1 + i\hbar\beta)\right\rangle \\
 &= -e^{-\beta\mu}G^<(\mathbf{r}_1 t_1 + i\hbar\beta, \mathbf{r}_2 t_2).
 \end{aligned} \tag{E.22}$$

Moreover, both propagators are homogenous in time³ and the time arguments can be replaced by their difference, i.e. $(t_1, t_2) \rightarrow (t_1 - t_2)$. The causal Green's function defined for complex time arguments then reads

$$G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) = \Theta[\Im(t_2 - t_1)] G^>(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) + \Theta[\Im(t_1 - t_2)] G^<(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) \tag{E.23}$$

and becomes quasi periodic along the imaginary time axis due to the Martin-Schwinger relation:

$$G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) = -e^{\beta\mu}G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2 - i\hbar\beta). \tag{E.24}$$

Hence it suffices to restrict the definition of the causal Green's function to purely imaginary time arguments. This transition from real to imaginary time arguments is also known as Wick rotation, in which the real time axis is rotated by $-\pi/2$ into the complex time plane and results in the transformation $(t_1 - t_2) \rightarrow i(t_1 - t_2)$ ⁴ [229]. It unifies the treatment of the time and temperature dependence of G . Within the intervall $|\Im(t_1 - t_2)| < \hbar\beta$, $G(t_1 - t_2)$ is quasi-periodic and one may express the causal Green's function as a Fourier series

$$G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) = -\frac{1}{i\hbar\beta} \sum_n \tilde{G}(\mathbf{r}_1, \mathbf{r}_2; z_n) e^{-iz_n(t_1 - t_2)}. \tag{E.25}$$

Due to the defined complex time domain and the Martin-Schwinger relation, the Fourier coefficients $\tilde{G}(z_n)$ are obtained by

$$\tilde{G}(\mathbf{r}_1, \mathbf{r}_2; z_n) = \int_0^{-i\hbar\beta} dt_1 G(\mathbf{r}_1, \mathbf{r}_2, t_1 - t_2) e^{iz_n(t_1 - t_2)} \tag{E.26}$$

³The statistical operator and the time evolution operator in Eq.(E.22) do commute. By use of the cyclic property of the trace, the time homogeneity can be proven.

⁴In the following, the time argument $t_1 - t_2$ is understood as complex valued and the imaginary unit is dropped.

⁵The proof of Eq.(E.26) makes use of the Martin-Schwinger relation, which reduces the integral to the upper or lower complex time domain.

Thereby, the complex frequencies z_n take only discrete values, the fermionic Matsubara frequencies, at which $\tilde{G}(z_n)$ becomes non-zero. These values are given by

$$\hbar z_n = \mu + i \frac{n\pi}{\beta} \quad n = \pm 1, \pm 3, \pm 5, \dots \quad (\text{E.27})$$

and coincide with the poles of the Fermi function [Eq.(E.10)] in the complex frequency domain. In case of a purely periodic function along the complex time axis, i.e. $f(t) = f(t - i\hbar\beta)$, the corresponding Fourier coefficients $\tilde{f}(\omega_n)$ are only defined at the bosonic Matsubara frequencies [60, 44, 48, 49]

$$\hbar \zeta_m = i \frac{m\pi}{\beta} \quad m = 0, \pm 2, \pm 4, \dots \quad (\text{E.28})$$

Based on Eq.(E.26) one may derive a spectral representation of the thermodynamic causal Green's function which can be cast in the form of

$$\tilde{G}(\mathbf{r}_1, \mathbf{r}_2; z_n) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \frac{A(\mathbf{r}_1, \mathbf{r}_2; \omega)}{z_n - \omega} \quad (\text{E.29})$$

and allows $\tilde{G}(z_n)$ to be continued either into the upper or lower complex frequency domain by $\tilde{G}(z_n) \rightarrow \tilde{G}(z)$. The fact, that both (half) complex planes serve as a continuation domain, is due to a common accumulation point $z_{\text{acc}} = \pm i\infty$ between the set of Matsubara frequencies $\{z_n\}$ and the domain $\{z \in \mathbb{C} : |\Im(z)| > 0\}$ ⁶. Hence, one can approach the real axis from above or from below, which in the limit yields the retarded or advanced Green's function at real frequencies. Thus one finds

$$G^{\text{ret/adv}}(\omega) = \lim_{\eta \rightarrow 0} \tilde{G}(\omega \pm i\eta), \quad (\text{E.30})$$

as it is also evident from Eq.(E.16). Due to the spectral function, $\tilde{G}(z)$ has a branch cut along the real frequency axis and shows a discontinuity there. This discontinuity is again given by the difference of the retarded and advanced Green's function from Eq.(E.30) and can be shown to yield the spectral function

$$A(\omega) = i \left[G^{\text{ret}}(\omega) - G^{\text{adv}}(\omega) \right]. \quad (\text{E.31})$$

The formalism of complex time arguments hence allows to obtain also a simple relation between the causal Green's function $\tilde{G}(z)$ and the spectral function $A(\omega)$ as for the case of vanishing temperatures where real time arguments are exploited.

⁶This is a consequence of the uniqueness of the analytic continuation from the complex analysis. See e.g. [230]

F. Four-point representation of the polarization function P from Hedin's equation

In the section about the microscopic response functions [Sec. 3.5.2] the polarization function P has been introduced as a two-point quantity within Hedin's equation [Eq.(3.109)]. As it shall be demonstrated now, it obeys a closed integral equation if formulated as a three-point or more general as a four-point quantity. Starting from the definition of $P(12)$ due to Eq.(3.105) one may rewrite this expression by introducing a delta function to obtain

$$P(12) = -i\hbar \int d3 \frac{\delta G(13; \mathcal{U})}{\delta \mathcal{U}_{\text{eff}}(2)} \delta(3 - 1^+) \Big|_{\mathcal{U}=0}. \quad (\text{F.1})$$

This manipulation allows to exploit Eq.(3.34) and yields

$$P(12) = -i\hbar \int d3 d4 \frac{\delta G(13; \mathcal{U})}{\delta \mathcal{U}_{\text{eff}}(2)} G^{-1}(34; \mathcal{U}) G(41^+; \mathcal{U}) \Big|_{\mathcal{U}=0}. \quad (\text{F.2})$$

The next step makes use of the chain rule of functional derivatives to the following expression

$$P(12) = -i\hbar \int d3 d4 d5 \frac{\delta G(13; \mathcal{U})}{\delta \mathcal{U}(5)} G^{-1}(34; \mathcal{U}) \frac{\delta \mathcal{U}(5)}{\delta \mathcal{U}_{\text{eff}}(2)} G(41^+; \mathcal{U}) \Big|_{\mathcal{U}=0}. \quad (\text{F.3})$$

In the equation above, the term $\frac{\delta G}{\delta \mathcal{U}_{\text{eff}}} G^{-1}$ can be rewritten due to the identity from Eq.(3.97). As an intermediate result the polarization function becomes

$$\begin{aligned} P(12) &= i\hbar \int d3 d4 G(13; \mathcal{U}) \frac{\delta G^{-1}(34; \mathcal{U})}{\delta \mathcal{U}_{\text{eff}}(2)} G(41^+; \mathcal{U}) \Big|_{\mathcal{U}=0} \\ P(12) &\stackrel{(3.112), (3.106)}{=} - \int d3 d4 P_0(1, 1^+, 4, 3) \Gamma(34; 2). \end{aligned} \quad (\text{F.4})$$

The final step involves the manipulation of the vertex function $\Gamma(12; 3)$ in such a way so that on the rhs of Eq.(F.4) the polarization function appears. This makes the explicit calculation of the functional derivative $\frac{\delta G^{-1}}{\delta \mathcal{U}_{\text{eff}}}$ necessary. Considering the equation of motion for the Green's function $G(\mathcal{U})$ [Eq.(3.99)], a Dyson equation such as Eq.(3.40) might be obtained as well:

$$G(12; \mathcal{U}) = G_0(12; \mathcal{U}) + \int d3 G_0(13; \mathcal{U}) \Sigma^{\text{xc}}(34; \mathcal{U}) G(42; \mathcal{U}). \quad (\text{F.5})$$

With the aid of the definition for the inverse Green's function [Eq.(3.34)], the Dyson equation for $G(\mathcal{U})$ can be rewritten in the following way

$$G^{-1}(12; \mathcal{U}) = G_0^{-1}(12; \mathcal{U}) - \Sigma^{\text{xc}}(12; \mathcal{U}) \quad (\text{F.6})$$

and allows to calculate the functional derivative that appears in the definition of the vertex function, explicitly. The inverse of the non-interacting Green's function $G_0^{-1}(12; \mathcal{U})$ is derivable in the same manner from the equation of motion for $G_0(\mathcal{U})$. This is simply given by Eq.(3.99) with $\Sigma^{\text{xc}} = 0$. Again, the inverse identity due to Eq.(3.34) applies and yields

$$G_0^{-1}(12; \mathcal{U}) = \left\{ i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 - V_{\text{ion}}(\mathbf{r}_1) - V_{\text{H}}(\mathbf{r}_1) - \mathcal{U}_{\text{eff}}(1) \right\} \delta(1-2). \quad (\text{F.7})$$

Hence, the vertex function [Eq.(3.106)] becomes

$$\begin{aligned} \Gamma(12; 3) &= \left. \frac{\delta G^{-1}(12; \mathcal{U})}{\delta \mathcal{U}_{\text{eff}}(3)} \right|_{\mathcal{U}=0} \\ &= -\delta(1-2)\delta(1-3) - \iint d4 d5 \frac{\delta \Sigma^{\text{xc}}(12; \mathcal{U})}{\delta G(45; \mathcal{U})} \frac{\delta G(45; \mathcal{U})}{\delta \mathcal{U}_{\text{eff}}(3)} \bigg|_{\mathcal{U}=0} \end{aligned} \quad (\text{F.8})$$

$$= -\delta(1-2)\delta(1-3) + \iint d4 d5 \Xi(2, 1, 4, 5) P(4, 5, 2, 2^+), \quad (\text{F.9})$$

while the chain rule has been applied additionally in Eq.(F.8) and in the last line the Eqs. (3.115), (3.105) and (3.113) have been used. Finally, with Eq.(F.4) and Eq.(F.9), the polarization $P(12)$ function, now expressed in a general four-point notation, becomes

$$P(1, 1^+, 2, 2^+) = P_0(1, 1^+, 2, 2^+) + \int d5 \dots d8 P_0(1, 1^+, 6, 5) \Xi(6, 5, 7, 8) P(7, 8, 2, 2^+). \quad (\text{F.10})$$

Without loss of generality, the transition from $1^+ \rightarrow 3$ can be performed and leads to a closed integral equation for the three-point function $P(1, 3, 2, 2^+)$ and similarly to a four-point function $P(1, 3, 2, 4)$ with the transition $2^+ \rightarrow 4$. In the latter case, the Bethe-Salpeter equation (3.114) is obtained.

G. Four-point representation of the density correlation function L

The derivation for the Bether-Salpeter equation of the density correlation function L is similar to the derivation presented in appendix F. Starting from Eq.(3.117), the introduction of the delta function $\delta(3 - 1^+)$ one may obtain with the definition of the inverse Green's function due to Eq.(3.34) the expression

$$L(12) = -i\hbar \int d3 d4 \frac{\delta G(13; \mathcal{U})}{\delta \mathcal{U}(2)} G^{-1}(34; \mathcal{U}) G(41^+; \mathcal{U}) \Big|_{\mathcal{U}=0}. \quad (\text{G.1})$$

With the aid of the identity given by Eq.(3.97), one further obtains

$$L(12) = i\hbar \int d3 d4 G(13; \mathcal{U}) \frac{\delta G^{-1}(34; \mathcal{U})}{\delta \mathcal{U}(2)} G(41^+; \mathcal{U}) \Big|_{\mathcal{U}=0} \quad (\text{G.2})$$

$$= \int d3 d4 L_0(1, 1^+, 4, 3) \Gamma'(34; 2), \quad (\text{G.3})$$

with the modified vertex function

$$\Gamma'(34; 2) = \frac{\delta G^{-1}(34; \mathcal{U})}{\delta \mathcal{U}(2)} \Big|_{\mathcal{U}=0}. \quad (\text{G.4})$$

Different from the vertex function Γ in Eq.(F.4), the functional derivative with respect to the external potential is required. Therefore, we make use of the Dyson equation

$$G(12; \mathcal{U}) = G_0(12; \mathcal{U}) + \int d3 G_0(13; \mathcal{U}) \Sigma(34; \mathcal{U}) G(42; \mathcal{U}) \quad (\text{G.5})$$

that results from the equation of motion [Eq.(3.99)], if the explicit expression for the effective potential [Eq.(3.100)] is substituted back into Eq.(3.99). Again, the inverse Green's function may be obtained similar to Eq.(F.6) from the Dyson equation (G.5)

$$G^{-1}(12; \mathcal{U}) = G_0^{-1}(12; \mathcal{U}) - \Sigma(12; \mathcal{U}), \quad (\text{G.6})$$

where the inverse non-interacting Green's function obeys the relation

$$G_0^{-1}(12; \mathcal{U}) = \left\{ i\hbar \frac{\partial}{\partial t_1} + \frac{\hbar}{2m_e} \nabla_{\mathbf{r}_1}^2 - V_{\text{ion}}(\mathbf{r}_1) - \mathcal{U}(1) \right\} \delta(1 - 2). \quad (\text{G.7})$$

Consequently, the vertex function Γ' can be evaluated explicitly to give the following expression

$$\Gamma'(12; 3) = \frac{\delta G^{-1}(12; \mathcal{U})}{\delta \mathcal{U}(3)} \Big|_{\mathcal{U}=0} \quad (\text{G.8})$$

$$= -\delta(1-2)\delta(1-3) - \iint d4 d5 \frac{\delta \Sigma(12; \mathcal{U})}{\delta G(45; \mathcal{U})} \frac{\delta G(45; \mathcal{U})}{\delta \mathcal{U}(3)} \Big|_{\mathcal{U}=0} \quad (\text{G.9})$$

$$= -\delta(1-2)\delta(1-3) + \iint d4 d5 \Xi'(2, 1, 4, 5) L(4, 5, 3, 3^+). \quad (\text{G.10})$$

In the equation above, the definition of the density correlation function L due to Eq.(3.117) and the definition of the kernel Ξ' due to Eq.(3.125) has been exploited. Finally, the combination of Eq.(G.3) and Eq.(G.10) yields the following integral equation

$$L(1, 1^+, 2, 2^+) = L_0(1, 1^+, 2, 2^+) + \int d5 \dots d8 L_0(1, 1^+, 6, 5) \Xi'(6, 5, 7, 8) L(7, 8, 2, 2^+). \quad (\text{G.11})$$

that, if taken transitions $1^+ \rightarrow 3$ and $2^+ \rightarrow 4$ are taken into account, yields the Bethe-Salpeter equation for the four-point density correlation function as given by Eq.(3.124).

H. Momentum representation of the microscopic dielectric function

Based on the definition of the microscopic dielectric function [Eq.(3.123)] we have in position space

$$\epsilon(\mathbf{r}_1, \mathbf{r}_2) = \delta(\mathbf{r}_1 - \mathbf{r}_2) - \int d\mathbf{r}_3 v(\mathbf{r}_1 - \mathbf{r}_3) P(\mathbf{r}_3, \mathbf{r}_2). \quad (\text{H.1})$$

Using the definition of the Fourier transform [Eq.(C.8)] one finds

$$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}_1} \epsilon(\mathbf{r}_1, \mathbf{r}_2) e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}_2} \quad (\text{H.2})$$

If we express the Coulomb kernel and the polarization function in terms of their inverse Fourier representation one obtains

$$\begin{aligned} \epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) &= \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}_1} \delta(\mathbf{r}_1 - \mathbf{r}_2) e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}_2} \\ &\quad - \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 \int d\mathbf{r}_3 e^{-i(\mathbf{q}+\mathbf{G})\mathbf{r}_1} \left[\frac{1}{V} \sum_{\mathbf{k}_2, \mathbf{G}_2} v(\mathbf{k}_2 + \mathbf{G}_2) e^{i(\mathbf{k}_2 + \mathbf{G}_2)(\mathbf{r}_1 - \mathbf{r}_3)} \right] \\ &\quad \times \left[\frac{1}{V} \sum_{\substack{\mathbf{k}_1, \\ \mathbf{G}_1, \mathbf{G}'_1}} e^{i(\mathbf{k}_1 + \mathbf{G}_1)\mathbf{r}_3} P(\mathbf{k}_1 + \mathbf{G}_1, \mathbf{k}_1 + \mathbf{G}'_1) e^{-i(\mathbf{k}_1 + \mathbf{G}'_1)\mathbf{r}_2} \right] e^{i(\mathbf{q}+\mathbf{G}')\mathbf{r}_2} \\ &= \delta_{\mathbf{G}, \mathbf{G}'} \\ &\quad - \sum_{\mathbf{k}_2, \mathbf{G}_2} \sum_{\substack{\mathbf{k}_1, \\ \mathbf{G}_1, \mathbf{G}'_1}} \delta_{\mathbf{q}, \mathbf{k}_2} \delta_{\mathbf{G}_2, \mathbf{G}} \delta_{\mathbf{q}, \mathbf{k}_1} \delta_{\mathbf{G}', \mathbf{G}'_1} \delta_{\mathbf{k}_1, \mathbf{k}_2} \delta_{\mathbf{G}_1, \mathbf{G}_2} v(\mathbf{k}_2 + \mathbf{G}_2) P(\mathbf{k}_1 + \mathbf{G}_1, \mathbf{k}_1 + \mathbf{G}'_1) \\ &= \delta_{\mathbf{G}, \mathbf{G}'} - v(\mathbf{q} + \mathbf{G}) P(\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}'). \end{aligned} \quad (\text{H.3})$$

I. Excitonic Hamiltonian

In section 4.1.7 we have introduced the excitonic Hamiltonian that shall be here derived. Within the Bloch representation of the density correlation function we have found the following expression from Eq.(4.46)

$$L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}(\zeta_l) = \frac{f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}})}{E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}} - \hbar\zeta_l} \left\{ \delta_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_4} \delta_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_3} + \sum_{\tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} \left[v_{\tilde{\mathbf{k}}'_8\tilde{\mathbf{k}}'_7} - W_{\tilde{\mathbf{k}}'_8\tilde{\mathbf{k}}'_7} \right] L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l) \right\}. \quad (\text{I.1})$$

Rearranging on the lhs and rhs and abbreviating the interaction terms by $I = v - W$ one finds

$$\begin{aligned} & \left[f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \right] \delta_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_4} \delta_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_3} \\ &= \left(E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}} - \hbar\zeta_l \right) L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3}(\zeta_l) - \sum_{\tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} \left[f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \right] I_{\tilde{\mathbf{k}}'_8\tilde{\mathbf{k}}'_7}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l) \\ &= \sum_{\tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} \left\{ \left(E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}} \right) \delta_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}'_7} \delta_{\tilde{\mathbf{k}}_3\tilde{\mathbf{k}}'_8} - \left[f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \right] I_{\tilde{\mathbf{k}}'_8\tilde{\mathbf{k}}'_7}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} - \hbar\zeta_l \delta_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}'_7} \delta_{\tilde{\mathbf{k}}_3\tilde{\mathbf{k}}'_8} \right\} L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l). \end{aligned} \quad (\text{I.2})$$

Introducing the identity matrix $\mathbb{1}$ within the Bloch representation reading $\mathbb{1}_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} = \delta_{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_2} \delta_{\tilde{\mathbf{k}}_3\tilde{\mathbf{k}}_4}$, Eq.(I.2) then becomes

$$\begin{aligned} & f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \mathbb{1}_{\tilde{\mathbf{k}}_4\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} \\ &= \sum_{\tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} \left\{ \left(E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}} \right) \mathbb{1}_{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} - \left[f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \right] I_{\tilde{\mathbf{k}}'_8\tilde{\mathbf{k}}'_7}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} - \hbar\zeta_l \mathbb{1}_{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} \right\} L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l). \end{aligned} \quad (\text{I.3})$$

From Eq.(I.3) we deduce the excitonic Hamiltonian

$$H_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} = \left(E_{\tilde{\mathbf{k}}_1}^{\text{qp}} - E_{\tilde{\mathbf{k}}_3}^{\text{qp}} \right) \mathbb{1}_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} - \left[f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \right] I_{\tilde{\mathbf{k}}_4\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} \quad (\text{I.4})$$

and thus find

$$f(E_{\tilde{\mathbf{k}}_1}^{\text{qp}}) - f(E_{\tilde{\mathbf{k}}_3}^{\text{qp}}) \mathbb{1}_{\tilde{\mathbf{k}}_4\tilde{\mathbf{k}}_2}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} = \sum_{\tilde{\mathbf{k}}'_7, \tilde{\mathbf{k}}'_8} \left[H_{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} - \hbar\zeta_l \mathbb{1}_{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}^{\tilde{\mathbf{k}}_1\tilde{\mathbf{k}}_3} \right] L_{\tilde{\mathbf{k}}_2\tilde{\mathbf{k}}_4}^{\tilde{\mathbf{k}}'_7\tilde{\mathbf{k}}'_8}(\zeta_l). \quad (\text{I.5})$$

J. Casida's equation

Given the expansion of the density in terms of the unperturbed Kohn-Sham orbitals [Eq.(5.69)], the reinsertion of this expression into Eq.(5.53) yields

$$\delta V_s(\mathbf{r}_1, \omega) = V_{\text{ext}}(\mathbf{r}_1, \omega) + \int d\mathbf{r}_2 f_{\text{Hxc}}(\mathbf{r}_1, \mathbf{r}_2; \omega) \left[\sum_{m', l'} \delta \rho_{m' l'}(\omega) \varphi_{m'}(\mathbf{r}_2) \varphi_{l'}^*(\mathbf{r}_2) \right]. \quad (\text{J.1})$$

In the following we need to obtain the corresponding matrix element of the induced Kohn-Sham potential. Like the density variation, δV_s is also a function of only one spatial variable and can be expressed in the same basis of products of Kohn-Sham orbitals such as $\delta \rho(\mathbf{r})$. Thus we can project both sides on a particular Kohn-Sham orbital pair to obtain:

$$\begin{aligned} \int d\mathbf{r}_1 \varphi_m^*(\mathbf{r}_1) \varphi_l(\mathbf{r}_1) \delta V_s(\mathbf{r}_1, \omega) &= \int d\mathbf{r}_1 \varphi_m^*(\mathbf{r}_1) \varphi_l(\mathbf{r}_1) \delta V_{\text{ext}}(\mathbf{r}_1, \omega) \\ &+ \sum_{m', l'} \left[\int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_m^*(\mathbf{r}_1) \varphi_l(\mathbf{r}_1) f_{\text{Hxc}}(\mathbf{r}_1, \mathbf{r}_2; \omega) \varphi_{m'}(\mathbf{r}_2) \varphi_{l'}^*(\mathbf{r}_2) \delta \rho_{m' l'}(\omega) \right] \end{aligned} \quad (\text{J.2})$$

The integral term on the left hand side is already given due to Eq.(5.69). We thus find

$$\delta \rho_{ml}(\omega) \left[\frac{\hbar\omega - (\varepsilon_m - \varepsilon_l)}{(f_l - f_m)} \right] = V_{\text{ext } ml}(\omega) + \sum_{m', l'} f_{\text{Hxc } ml, m' l'}(\omega) \delta \rho_{m' l'}(\omega) \quad (\text{J.3})$$

and finally after rearranging individual terms

$$\begin{aligned} \sum_{m', l'} \left\{ \left[\frac{\hbar\omega - (\varepsilon_m - \varepsilon_l)}{(f_l - f_m)} \right] \delta_{m, m'} \delta_{l, l'} - f_{\text{Hxc } ml, m' l'}(\omega) \right\} \delta \rho_{m' l'}(\omega) \\ = V_{\text{ext } ml}(\omega) \delta \rho_{ml}(\omega). \end{aligned} \quad (\text{J.4})$$

Since the pair of indices (ml) and $(m'l')$ survive only for pairs of occupied and unoccupied orbitals and vice versa, we obtain a set of two coupled equations that read

$$\begin{aligned} \sum_{j, b} \left(\left\{ [-\hbar\omega + (\varepsilon_i - \varepsilon_a)] \delta_{i, j} \delta_{a, b} - \mathcal{K}_{ia, jb}(\omega) \right\} \delta \rho_{jb} - \mathcal{K}_{ia, bj}(\omega) \delta \rho_{bj} \right) \\ = V_{\text{ext } ia}(\omega) \delta \rho_{ia}(\omega) \end{aligned} \quad (\text{J.5})$$

$$\begin{aligned} \sum_{j, b} \left(-\mathcal{K}_{ai, jb}(\omega) \delta \rho_{jb}(\omega) + \left\{ [\hbar\omega - (\varepsilon_a - \varepsilon_i)] \delta_{a, b} \delta_{i, j} - \mathcal{K}_{ai, bj}(\omega) \right\} \delta \rho_{bj} \right) \\ = V_{\text{ext } ai}(\omega) \delta \rho_{ai}(\omega). \end{aligned} \quad (\text{J.6})$$

To be consistent with section 5.4, we have used the abbreviation for the four-orbital integral as given by Eq.(5.66). Both equations, J.5 and J.6 allow for a compact notation in terms of a matrix equation,

$$\left[\begin{pmatrix} \mathbf{A}(\omega) & \mathbf{B}(\omega) \\ \mathbf{B}(\omega) & \mathbf{A}(\omega) \end{pmatrix} - \hbar\omega \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix} \right] \begin{pmatrix} \delta\boldsymbol{\rho}(\omega) \\ \delta\boldsymbol{\rho}^*(\omega) \end{pmatrix} = \begin{pmatrix} \mathbf{V}_{\text{ext}}(\omega) \\ \mathbf{V}_{\text{ext}}^*(\omega) \end{pmatrix} \quad (\text{J.7})$$

where the submatrices $\mathbf{A}(\omega)$ and $\mathbf{B}(\omega)$ are identical with Eqs. (5.67) and (5.68). The vector notation of the density variation and the external potential is meant to be within the space of Kohn-Sham transition pairs, whereas the complex conjugate is associated with the interchange of the index pair, i.e. $\delta\rho_{lm} = \delta\rho_{ml}^*$.

K. Matrix elements of the perturbed Fock operator

We derive the explicit expression for the matrix elements $H_{\text{nl},mn}^{(1)}(\omega)$ of the nonlocal part of the perturbed sc Hamiltonian given in the frequency domain. First, considering the Fock operator [Eq.(8.31)] the Fourier transform simply reads

$$H_{\text{nl}}(\mathbf{r}, \mathbf{r}', \omega) = \frac{\rho(\mathbf{r}, \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|}. \quad (\text{K.1})$$

Second, the variation of Eq.(K.1) w.r.t. the density matrix at a fixed frequency ω can be calculated using standard techniques of functional derivatives:

$$\begin{aligned} \frac{\delta H_{\text{nl}}[\rho(\mathbf{r}, \mathbf{r}', \omega)]}{\delta \rho(\mathbf{y}, \mathbf{y}', \omega)} &= \lim_{\epsilon \rightarrow 0} \frac{H_{\text{nl}}[\rho(\mathbf{r}, \mathbf{r}', \omega) + \epsilon \delta(\mathbf{r} - \mathbf{y})\delta(\mathbf{r}' - \mathbf{y}')] - H_{\text{nl}}[\rho(\mathbf{r}, \mathbf{r}', \omega)]}{\epsilon} \\ &= \lim_{\epsilon \rightarrow 0} \frac{\rho(\mathbf{r}, \mathbf{r}', \omega) + \epsilon \delta(\mathbf{r} - \mathbf{y})\delta(\mathbf{r}' - \mathbf{y}')}{\epsilon |\mathbf{r} - \mathbf{r}'|} - \frac{\rho(\mathbf{r}, \mathbf{r}', \omega)}{\epsilon |\mathbf{r} - \mathbf{r}'|} \\ &= \frac{\delta(\mathbf{r} - \mathbf{y})\delta(\mathbf{r}' - \mathbf{y}')}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (\text{K.2})$$

Thus the variation of the nonlocal part of the sc Hamiltonian is calculated by integrating over the density matrix variation:

$$\begin{aligned} H_{\text{nl}}^{(1)}(\mathbf{r}, \mathbf{r}', \omega) &\equiv \delta H_{\text{nl}}(\mathbf{r}, \mathbf{r}', \omega) = \int d\mathbf{y} d\mathbf{y}' \frac{\delta(\mathbf{r} - \mathbf{y})\delta(\mathbf{r}' - \mathbf{y}')}{|\mathbf{r} - \mathbf{r}'|} \delta \rho(\mathbf{y}, \mathbf{y}', \omega) \\ &= \frac{\delta \rho(\mathbf{r}, \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} \\ &\equiv \frac{\rho^{(1)}(\mathbf{r}, \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|}. \end{aligned} \quad (\text{K.3})$$

From Eq.(K.3) we calculate the corresponding matrix elements as

$$H_{\text{nl},mn}^{(1)}(\omega) = \int d\mathbf{r} d\mathbf{r}' \varphi_m^{*0}(\mathbf{r}) \varphi_n^0(\mathbf{r}') \frac{\rho^{(1)}(\mathbf{r}, \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|}, \quad (\text{K.4})$$

where $\rho^{(1)}(\mathbf{r}, \mathbf{r}', \omega)$ is the frequency dependent first order density matrix response and $\varphi_n(\mathbf{r})$ denote the stationary orbitals of Eq.(8.29).

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Danksagung

Die Anfertigung dieser Arbeit mag als die Kondensation alle Anstrengungen und Herausforderungen gesehen werden, welche sich im Laufe dieses Studiums als täglicher Begleiter eingereiht haben. Für die Unterstützung und das Gelingen meiner Dissertation möchte ich mich bei allen Kollegen der Arbeitsgruppe *Computational Materials Physics* bedanken.

Besonderen Dank gilt meinem Betreuer Prof. Georg Kresse, der mir mit Rat und Tat regelmässig zur Seite stand.

Zudem bin ich sehr froh in meinen beiden Kollegen Dr. Menno Bokdam und Dr. Emanuele Maggio zwei Personen gefunden zu haben, mit denen ein stets offener Gedankenaustausch möglich war. In diesem Zusammenhang, soll auch Dr. Martijn Marsman erwähnt werden, der mit seiner angenehmen und ruhigen Art auch themenübergreifend ein oft gern gesuchter Ansprechpartner war.

Des Weiteren gilt auch ein grosser Dank an Katharina Simma, Dr. Doris Hecht-Aichholzer, sowie Dr. Doris Vogtenhuber, die mir in vertrauensvollen Gesprächen auch mal auf die Schulter klopfen.

Zu guter Letzt, und doch am Wichtigsten, war und ist meine kleine Familie, Daniela und Maximilian. Danke, dass ihr da seid! Ihr seid meine Basis, habt mich stets angetrieben und Rückhalt gegeben. Dank gilt auch meinen Eltern und meinem Bruder, die mich mit allen Ihren Möglichkeiten unterstützt haben.

Abstract

The research of novel materials or material compounds is important in the field of material science. Many of these materials have found applications in industrial products. Theoretical methods that make predictions on electronic and optical properties are essential in the search of these new materials. The solution of the underlying many-body problem is traditionally tackled with the aid of ab-initio calculations. Hereby, one aims to solve the many-body Hamiltonian in a parameter-free approach. With the aid of these methods a rigorous description of real materials can be achieved.

Density functional theory (DFT) is one of the most applied methods to calculate electronic properties and in the framework of time-dependent functional theory (TDDFT), even optical properties can be calculated. Like all theories, they are as good as the involved approximations, may it be for the exchange-correlation potential in DFT or for the exchange-correlation kernel in TDDFT. The field theoretical approach gives a rigorous access to the many-body problem and allows to close the gap between results from DFT/TDDFT and experiment. Moreover, it yields results that can be compared to real experiments such as (inverse)photoemission.

In this thesis neutral excitations due to photoabsorption process are investigated. The quantity of interest, is the macroscopic dielectric function that is obtained from the polarization function. The latter is usually calculated from a closed integral equation of four-point quantities, denoted as the Bethe-Salpeter equation (BSE). As this method involves the solution of an in general non-Hermitian eigenvalue problem (EVP), one reduces the entire EVP to a Hermitian one. This is known as the Tamm-Dancoff approximation (TDA). In this work, we answer the question how the optical absorption spectrum changes when going beyond the TDA and what kind of materials show a pronounced difference between both approaches. Furthermore, the macroscopic dielectric function is also solved for finite momentum transfer, different to the optical absorption that happens at the long wave length limit.

The second part of this thesis covers the implementation of the real time evolution (TE) of orbitals. This method yields exactly the same optical spectrum, but with less computational effort. Therefore, it is the method of choice when dealing with amorphous or large scale systems, involving many atoms in the unit cell.

Abstract

Die Erforschung neuer Materialien oder neuer Verbindungen ist eines der Schwerpunkte in der Materialwissenschaft, da diese Materialien oft Anwendung in der Industrie finden. Die Suche nach solchen neuen Materialien wird durch theoretische Methoden unterstützt. Dabei steht die Lösung des Vielteilchen-Problems an erster Stelle welches mit Hilfe von ab-initio Rechnungen gelöst wird. Diese Methode erlaubt eine genaue Beschreibung von echten Materialien.

Eine der am häufigsten verwendeten Methode ist die Dichtefunktionaltheorie (DFT) um elektronische Eigenschaften zu berechnen. Optische Eigenschaften können sogar im Rahmen der zeitabhängigen DFT (TDDFT) berechnet werden. Wie alle Theorien, sind ihre Ergebnisse nur so gut wie es ihre Approximation erlaubt. Im Fall der DFT betrifft dies das Austausch-Korrelations Potential sowie den Austausch-Korrelation Kernel in der TDDFT. Im Gegensatz dazu, ermöglicht die feldtheoretische Beschreibung einen direkten Zugang zum Vielteilchen-Problem und schliesst die Lücke zwischen Ergebnissen aus der DFT/TDDFT und dem Experiment. Zudem können in diesem Fall Ergebnisse mit echten realen Experimenten wie z.B. der (inversen) Photoemission verglichen werden.

In dieser Arbeit, interessieren wir uns jedoch für neutrale Anregungen, wie der Photoabsorption. Die dabei interessante Grösse ist die makroskopische dielektrische Funktion, welche mit Hilfe der Polarisationsfunktion berechnet werden kann. Letztere wird gewöhnlich aus der Lösung einer geschlossenen Integral-Gleichung, der Bethe-Salpeter Gleichung (BSE) gewonnen. Diese Methode bedarf im Allgemeinen der Lösung eines nicht-hermiteschen Eigenwertproblems (EVP), welches sich im Rahmen der Tamm-Dancoff Approximation (TDA) zu einem hermiteschen EVP reduziert. In dieser Arbeit soll die Frage beantwortet werden, inwiefern sich das optische Spektrum ändert, wenn man über die TDA hinausgeht. Des Weiteren wird die makroskopische dielektrische Funktion auch für endliche Wellenvektoren berechnet, im Gegensatz zum optischen Spektrum an verschwindenden Wellenvektoren.

Der zweite Abschnitt dieser Arbeit betrifft die Implementierung der Methode zur Echtzeitpropagation von Orbitalen. Diese Methode erlaubt es ebenfalls das optische Spektrum zu berechnen, jedoch mit einem geringeren Rechenaufwand. Daher kann diese Methode als Alternative betrachtet werden, wenn amorphe Systeme oder Systeme mit einer grossen Anzahl von Atomen in der Einheitszelle berücksichtigt werden müssen.