Ab Initio Study of Density Functional Theory from the Perspective of the Green’s Function Formalism.

(Ab initio studie van Dichtheidsfunctioonaltheorie op basis van Greense functie technieken.)

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Leonardo da Vinci (1455-1517)
Voorwoord

Hoewel een voorwoord meestal als laatste onderdeel geschreven wordt, is het zeker niet het minst belangrijke van deze scriptie. Niet alleen beheert dit stukje wellicht tot één van de meest gelezen onderdelen, het stelt me vooral in staat enkele mensen te bedanken die een speciale rol hebben gespeeld in mijn onderzoek van de voorbije vier jaar.

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List of common symbols and abbreviations.

\( \hat{H} \) hamiltonian of the system (in second quantization)
\( \hat{T} \) kinetic energy (in second quantization)
\( \hat{V} \) one-body potential (in second quantization)
\( \hat{W} \) two-body interaction (in second quantization)
\( | 0(A) \rangle \) ground-state wave function of many-body system with \( A \) particles
\( G_{\alpha\beta}(E) \) (one-body) Green’s function in configuration-energy space
\( \Sigma(E) \) (irreducible) self-energy
\( I \) first-ionization energy
\( A \) electron affinity
\( \rho(\vec{r}) \) or \( \rho_0(\vec{r}) \) (one-body) density (of the ground state)
\( E[\rho] \) total-energy functional in the density
\( E_{xc}[\rho] \) exchange-correlation functional in the density
\( T[\rho] \) kinetic energy of interacting system
\( T_d[\rho] \) kinetic energy of noninteracting system
\( T_{cl}[\rho] \) kinetic contribution to exchange-correlation energy
\( v_{xc}(\vec{r}) \) exchange-correlation potential
\( | \Psi \rangle \) or \( | \Phi_0 \rangle \) (ground-state) wave function of the interacting many-body
wave function
\( | \Phi \rangle \) or \( | \Phi_0 \rangle \) (ground-state) wave function of the noninteracting many-body
wave function

DFT Density Functional Theory
s.p. single-particle
HF Hartree-Fock
Dyson(1) self-consistent scheme to solve Dyson’s equation of first order in the
two-body interaction (i.e. the Hartree-Fock equation)
Dyson(2) self-consistent scheme to solve Dyson’s equation of second order in the
two-body interaction
BAGEL Basis GEnerated by Lanczos
HK Hohenberg-Kohn
xc exchange-correlation
KS Kohn-Sham
Chapter 1

Introduction.

Many-body problems have a special place in physics because many practical problems deal with assemblies involving a lot of particles. As is well-known, these systems are much more complicated than systems with only a few particles due to the increase of the phase space which is available to the particles. Therefore, we have to resort to approximative methods.

These methods can be classified according to the level of empirical influence that is allowed in the theoretical description. When the formalism is based purely on the microscopic interaction between the particles, the corresponding theory is labeled \textit{ab initio}. Other methods are termed \textit{semi-empirical} and \textit{empirical} methods. Both classes depend on experimental information to start the scheme, but to a different extent. Algorithms in the former class start from an input expression that is constructed based on \textit{ab initio} grounds, but which involves some parameters that are fitted to experiment. Empirical methods are derived totally on experimental grounds, which reduces the predictive power of the method.

In this thesis, we will combine two powerful many-body techniques which are applied to quantum-mechanical systems. The first one, the \textit{Green's function formalism}, is a purely \textit{ab initio} method, based on a microscopic approach. The second one is \textit{Density Functional Theory (DFT)}, which, depending on the situation, belongs to the class of the \textit{ab initio} schemes or to the group of semi-empirical methods. The Green’s function formalism and DFT are usually applied to different types of systems. It is the goal of this work to study systems to which both schemes can be applied. In this way, we can use the \textit{ab initio} foundations of the Green’s function scheme to gain insight in the semi-empirical input that is required in DFT. We will now sketch briefly which are the basic ideas of both the Green’s function method and DFT.

The Green’s function formalism, to be discussed in chapter 2, describes a many-body system by means of a single-particle Green’s function, which follows the propagation of a particle in the interacting many-body system. From the Green’s function
used in this work, all important observables of the many-body assembly can be calculated. In this way a purely theoretical and microscopic description can be made of the quantum system, but it is of course a very hard and computationally expensive way to study a many-body system. This is the reason why the application area of the Green’s function method is restricted to systems with a high degree of symmetry, such as nuclear matter, nuclei, the electron gas, atoms, and solids. The Green’s function of a particle (or of a hole) can be obtained by solving Dyson’s equation. This equation involves a special operator, the self-energy, which models all interactions that the particle has with the other particles of the system. The self-energy is a non-local (in coordinate space) and energy-dependent (in energy space) operator. Because of its complexity, the self-energy is most often expanded in a series in the two-body interaction (in our case the Coulomb potential between the electrons) and truncated at order \( n \). The truncated expansion is then substituted in Dyson’s equation and we call the result the Dyson’s equation of order \( n \). As will be discussed in chapter 2, the truncated self-energy also depends on the Green’s function we are looking for. Therefore, the solution of Dyson’s equation up to order \( n \) should be performed in a self-consistent way (see chapters 3 and 4). First we make some initial guess for the Green’s function of the interacting system (e.g. based on the Green’s function of the hydrogen-like system, which can be solved exactly), which we use to evaluate the self-energy truncated at order \( n \). This self-energy is substituted in Dyson’s equation, which is solved to find an update for the Green’s function. This update is then used to reevaluate the self-energy, which can again be put into Dyson’s equation. The cycle is repeated until the Green’s function of some iteration (almost) coincides with the Green’s function of the previous iteration. Of course, the more terms are taken into account in the self-energy expansion, the more accurate the description of the many-body system will be but also the more expensive the calculations become. The self-consistent approach complicates the solution scheme as well, but it ensures that the convergent solution is independent of the ansatz used to start the scheme and that some conservation rules are obeyed (such as the conservation of the number of particles). In this work, we truncate the self-energy at second order and the resulting Dyson equation is solved for closed-shell (chapter 3) and open-shell (chapter 4) atomic systems. Atoms are a good choice for the purposes of this work because these systems can be studied using both Green’s function theory and DFT (other possibilities would be the electron gas and condensed matter). As a result, we are in a position to make an (almost) exact description of the sample systems using Green’s functions and learn something about the quality of the description of the same systems using DFT. We will now focus on the scheme that DFT uses to study many-body systems.

Density Functional Theory uses the single-particle (s.p.) ground-state density as a central variable, as opposed to the Green’s function in the previous scheme or the total wave function of the system as in standard quantum mechanics. As will be discussed in chapter 5, it can be proven that by this choice no information is lost,
although the s.p. density only involves three variables (spatial coordinates), where
the total wave function depends on $3N$ variables ($N$ is the number of particles in the
system). In this way, DFT is capable of tackling intricate systems, such as molecules
consisting of a large number of atoms, without any degree of symmetry. As a re-
result, DFT is applied in a variety of molecular modeling problems. In particular, we
mention the simulation of petrochemical processes by means of quantum chemistry
which allows for a full understanding of the reaction pattern. This knowledge can
then be used to optimise the process. Another example is situated in the field of
pharmacology, where new medicines are designed by means of computer simulation
instead of by actually producing the prototype molecules. As a final example, we
also mention topics in biotechnology such as the study of proteins which are essen-
tial for the regulation of biological systems (e.g. dopamine) and the description of
damage and repair mechanisms in DNA sequences.

From the s.p. density, all other observables of the many-body system can be calcu-
lated as a functional in the density. Within the DFT formalism, the ground-state
density can be obtained by solving the Euler-Lagrange equation, which variationally
minimizes the total energy of the system over all s.p. densities that may occur in the
system. However, the practical way to perform a DFT calculation uses the Kohn-
Sham (KS) scheme, which consists of a system of Schrödinger-like equations involving
only one-body operators. These equations are constructed such that their solutions
(the KS orbitals) result in the correct s.p. density of the interacting system. The KS
scheme gives DFT its computational speed by introducing the exchange-correlation
(xc) potential, which is a one-body potential that in principle includes all two-body
effects present in the interacting system. Within DFT, the xc potential is defined as
the functional derivative of the xc functional. According to the theory, this xc func-
tional is universal, i.e. it is the same for all systems in which the particles interact
via the Coulomb potential (such as an atom, a molecule, or a solid). Unfortunately,
DFT does not give clues on how to construct this universal functional. At the very
best, merely some sum rules for the exact xc functional and potential are derived.
Therefore, in practice, approximate functionals are used which include the exchange
and correlation effects in the many-body system to some extent. Very often, these
functionals are derived on semi-empirical grounds, e.g. starting from the expansion
of the total energy per particle for the homogeneous electron gas. Then parameters
are added to this expansion, which can be determined in two ways. Mostly, the
functional parameters are fitted to energetic data of a large training set of atoms,
ions, and molecules. For some functionals, the parameter set is chosen such that
(some of) the basic sum rules for the exact xc functional are obeyed. The latter
way of constructing functionals is of course much more satisfying from a theoreti-
cal point of view because it is an ab initio approach: universal functionals should be
constructed on universal grounds. Therefore, it is interesting to construct the xc
potential by means of methods other than DFT for some simple test systems. In
this way, we can assess the quality of existing functionals and learn what kind of
correlations are embedded in the various approximative forms.

The central theme of this work is now the following: we calculate the s.p. ground-state density for some atomic systems by means of the Green’s function method. We then need to find the xc potential that DFT would require to generate the same s.p. density (this is the so-called inversion problem). In chapter 6, we will discuss a new algorithm to perform this inversion process. Once the inversion problem is solved, we exactly know what kind of correlation effects are included in the xc potential (namely those of the advanced Green’s function scheme). These exact potentials can be used e.g. in a refit of existing functionals or in the construction of a new functional based on \textit{ab initio} grounds. In this way, the Green’s function calculations can provide DFT with a more microscopic basis and can lead to a more systematic approach in the construction of new functionals.

Parts of this thesis have been published in international papers, see Ref. [1].
Chapter 2

The Green’s function formalism.

2.1 Introduction.

Over the years, a variety of techniques to study a many-body system have been developed. One of the methods that is very often used is Density Functional Theory (DFT), which will be discussed extensively in chapter 5. DFT has the advantage of being computationally very efficient, such that extremely complex molecules can be tackled, but it misses the ability to examine the many-particle ensemble in a detailed fashion. The most obvious way to study a many-body system on a microscopic scale is to concentrate on how a single particle propagates through the interacting system. Depending on the nature of the interaction present, this microscopic study can or cannot be performed using perturbative theory. For common many-body systems governed by the Coulomb force such as atoms, molecules, and solids, a perturbative method as presented by the Green’s function formalism is very well suited. In this scheme, we use a rather abstract concept, namely the single-particle Green’s function or propagator to observe a particle moving around in the interacting medium. Depending on the order at which we truncate the perturbation series of the Green’s function scheme, more or less interactions (collisions) of the particle with the other particles are taken into account. It is clear that this method will not be as fast as e.g. DFT, such that only simple systems (atoms and small molecules) can be considered if we want to take into account several orders in the perturbation series. In a first-order calculation, we try to include the main part of the two-body interactions in the system by taking some average over the forces between the particles in the assembly. This first-order approach is also known as the Hartree-Fock approximation and it is surprising that a rather rough method which averages the two-body interaction into a one-body potential, produces a good description in many cases. However, as computational means increase and the nature of the applications change, we want to include effects beyond Hartree-Fock. The higher-order terms in the perturbation series gradually include more complex interactions
and give a more detailed picture of the many-body system under study. In this work, we will consider only the first- and second-order term in the series of the Green’s function. As will be demonstrated, this approximation already provides an accurate description for light atoms.

Once the Green’s function of a system has been determined, the expectation value of any one-body operator in the ground state of that system (e.g. the one-particle density) can be found typically by performing a contour integration that involves the Green’s function. As we will see, the total energy (a two-body quantity) can be found using the single-particle Green’s function as well. Another reason to study Green’s functions is that we exactly know what kind of Feynman diagrams are embedded in each term in the perturbation series. This is of key importance to establish a microscopic background of Density Functional Theory by means of the Green’s function formalism (see chapter 6 for details on how the connection between the two schemes is made).

Because of the importance of the subject for theoretical many-body physics, reviews on the Green’s function method are largely available (see e.g. [2], [3], and [4]). How the formalism is applied more specifically to quantum chemistry can be found in e.g. references [5]-[10].

2.2 One-particle picture.

As indicated in the introduction, the main use of the Green’s function lies within a many-particle context. Nevertheless, it is interesting to see how the Green’s function appears in a natural way when studying the propagation of a single particle in an external field, i.e. we want to study a system consisting of only one particle by means of a Green’s function. Suppose that we have a particle described by a state $|\Psi(t')\rangle$ at some time $t'$. Under influence of the hamiltonian $h_0$ of the system, the evolution of the state of the particle will be given by the solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = h_0 |\Psi(t)\rangle,$$

represented by (assuming that the hamiltonian is time-independent)

$$|\Psi(t)\rangle = e^{-i\hbar h_0 (t-t')} |\Psi(t')\rangle \quad t > t'.$$  \hspace{1cm} (2.2)

We are only interested in the forward time propagation and therefore we restrict to times $t$ larger than the initial time $t'$. Projecting to coordinate space, we obtain

$$\Psi(x, t) = \langle x |\Psi(t)\rangle$$

$$= \langle x | e^{-i\hbar h_0 (t-t')} |\Psi(t')\rangle$$

$$= \int dx' \langle x | e^{-i\hbar h_0 (t-t')} | x' \rangle \langle x' |\Psi(t')\rangle$$
2.2. One-particle picture.

\[ = i \int dx' G(x, x', t - t') \Psi(x', t') \quad t > t'. \quad (2.3) \]

Here, we adopted the convention that \( x \) stands for the coordinate-space vector \( r' \) combined with the spin degree of freedom \( s \). We see that the state of the particle at any time \( t > t' \) can be obtained from a single function, the so-called Green’s function

\[ G(x, x', t - t') = -i \langle x | e^{-\frac{i}{\hbar} \hat{H}(t-t')} | x' \rangle \theta(t-t'). \quad (2.4) \]

The step function \( \theta(t-t') \) expresses that we are only interested in forward time propagation. It is also clear that information about the particle in all places \( x' \) at time \( t' \) is required to find the state in coordinate \( x \) at time \( t \). This is familiar from the theory of wave propagation: every point on a wave front at some time contributes to every point of the wave front at a later time (Huygens’ principle). We see that the Green’s function describes how the system propagates from coordinate \( x' \) at \( t' \) to \( x \) at \( t \), and therefore it is also called the single-particle propagator.

Apart from the representation in coordinate-time space, the Green’s function can be represented in whatever complete basis set \( \{ \psi_\alpha \} \) (where \( \alpha \) represents all quantum numbers necessary to specify the particle in the chosen basis, e.g. the principal quantum number \( n \) and orbital angular momentum \( l \) in case of a basis set from a hydrogen-like system). Inserting this complete set twice, we obtain from Eq. (2.4)

\[ G(x, x', t - t') = -i \sum_{\alpha, \beta} \langle x | \psi_\alpha \rangle \langle \psi_\alpha | e^{-\frac{i}{\hbar} \hat{H}(t-t')} | \psi_\beta \rangle \langle \psi_\beta | x' \rangle \theta(t-t') \]

\[ = \sum_{\alpha, \beta} \psi_\alpha(x) \quad \psi_\beta(x') \quad G_{\alpha\beta}(t - t'). \quad (2.5) \]

Consequently, the Green’s function in configuration space assumes the form:

\[ G_{\alpha\beta}(t - t') = -i \langle \psi_\alpha | e^{-\frac{i}{\hbar} \hat{H}(t-t')} | \psi_\beta \rangle \quad \theta(t-t'). \quad (2.6) \]

Turning from the time domain to the energy representation by means of a Fourier transform we obtain:

\[ G_{\alpha\beta}(E) = \int_{-\infty}^{\infty} dt(t-t') \quad e^{\frac{i}{\hbar} E(t-t')} \quad G_{\alpha\beta}(t - t') \]

\[ = -i \int_{-\infty}^{\infty} dt(t-t') \quad e^{\frac{i}{\hbar} E(t-t')} \quad \langle \psi_\alpha | e^{-\frac{i}{\hbar} \hat{H}(t-t')} | \psi_\beta \rangle \quad \theta(t-t') \]

\[ = \langle \psi_\alpha | \int_{-\infty}^{\infty} d\omega \quad \frac{\delta(\omega - \frac{E - E_\alpha}{E_\beta})}{\omega + i\eta} \quad | \psi_\beta \rangle \]

\[ = \langle \psi_\alpha | \frac{1}{\frac{E - E_\alpha}{E_\beta} + i\eta} \quad | \psi_\beta \rangle, \quad (2.7) \]
where we have used the following representations of step- and deltafunctions:

\[
\theta(t - t') = -\int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} \frac{e^{-i\omega(t-t')}}{\omega + i\eta},
\]

\[
\delta(\omega) = \int_{-\infty}^{\infty} \frac{d(t - t')}{2\pi} e^{-i(t-t')\omega}.
\] (2.8)

Concerning the evaluation of the integral in the step function by means of complex contour integration, we note that for \( t > t' \) we have to close the contour \( C \) in the lower half plane (lemma of Jordan), where due to the infinitesimally small (but positive) parameter \( \eta \), we obtain unity. For \( t < t' \), the contour should be closed in the upper half plane and the expression evaluates to zero.

We will now derive by means of perturbation theory how we can find the Green’s function of system with one particle from the Green’s function of another system containing one particle as well. Although it is not necessary for a one-particle system to advocate perturbation theory (the problem can be solved exactly), it is interesting to consider this case because perturbation theory is indispensable in a many-particle context, which will be discussed later on. If we decompose the hamiltonian \( h_0 \) as \( h_0 = h_0^{(0)} + h_0^{(1)} \), where \( h_0^{(1)} \) is a perturbation to \( h_0^{(0)} \) (e.g. a change in the external field), we can use of the operator identity

\[
\frac{1}{A - B} \equiv \frac{1}{A} + \frac{1}{B} \frac{1}{A - B}
\] (2.9)

to arrive at a perturbation expansion for the Green’s function:

\[
\langle \psi_\alpha | \frac{\hat{h}}{E - h_0 + i\eta} | \psi_\beta \rangle = \langle \psi_\alpha | \frac{\hat{h}}{E - h_0^{(0)} + i\eta} | \psi_\beta \rangle + \sum_{\alpha'\beta'} \langle \psi_\alpha | \frac{\hat{h}}{E - h_0^{(0)} + i\eta} | \psi_{\alpha'} \rangle \langle \psi_{\alpha'} | \frac{h_0^{(1)}}{h} | \psi_{\beta'} \rangle \langle \psi_{\beta'} | \frac{\hat{h}}{E - h_0 + i\eta} | \psi_\beta \rangle,
\] (2.10)

or with the introduction of \( G_{\alpha\beta}^{(0)}(E) = \langle \psi_\alpha | \frac{\hat{h}}{E - h_0^{(0)} + i\eta} | \psi_\beta \rangle \)

\[
G_{\alpha\beta}(E) = G_{\alpha\beta}^{(0)}(E) + \sum_{\alpha'\beta'} G_{\alpha\alpha'}^{(0)}(E) \langle \psi_{\alpha'} | \frac{h_0^{(1)}}{h} | \psi_{\beta'} \rangle G_{\beta'\beta}(E).
\] (2.11)

A similar equation can be derived in a many-particle context, as discussed in section 2.4.

As a concluding remark, we note that the introduction of the infinitesimal parameter \( \eta \) in Eq. (2.7) is an elegant way to indicate where the contour should be closed when performing contour integrations with Green’s functions. These infinitesimal
terms assume a similar role as the infinitesimal arcs on the real axis one introduces
to avoid real poles during complex contour integrations (see e.g. [11] for a more
detailed discussion). However, we can also give a physical interpretation to the Green’s
function based on the infinitesimal term $\eta$: Eq. (2.7) involving $+i\eta$ describes a particle
propagating forward in time. In the system that was considered here, only
particle propagation is of relevance, but in a many-body context, propagation of
particles and holes is to be put on an equal footing. To explain this in more detail,
let us consider a many-body system in which the particles are moving independently
(single-particle motion). This system is described by a Hamiltonian which is the sum
of the Hamiltonians of each of the particles individually: $H_0 = \sum_{i=1}^A h_0(i)$ (where $A$
the number of particles in the system). To obtain a proper antisymmetrization,
the ground state $|0(A)\rangle$ of this noninteracting many-particle system is described by
a Slater determinant $|\Phi_0\rangle$ composed of the lowest-lying single-particle orbitals of
the system (found by solving the Schrödinger equation corresponding to $H_0$). The
Green’s function will now involve both particle and hole propagation and will therefore
consist of two terms, one involving an infinitesimal term $+i\eta$ and one with a
term $-i\eta$. A good example of a noninteracting many-body system is the Hartree-
Fock model. This model will be discussed at the end of section 2.4, in which we
provide a more detailed analysis of Green’s function techniques.

### 2.3 Green’s functions in interacting many-body systems.

In this and in the next section, we will have a more in-depth look into the Green’s
function formalism and explain how Green’s functions can describe an interacting
system consisting of many particles by means of perturbation theory. Although the
Green’s function formalism is applicable to any many-body system, we will focus
throughout the discussion on many-electron systems.

When dealing with many-particle objects it is advantageous to work in a second-
quantization scheme. The Hamiltonian of a many-body system governed by a two-
boby interaction $W$ then reads (we distinguish operators in second quantization
from those in first quantization by an operator hat)

$$
\hat{H} = \hat{H}_0 + \hat{W} = \int dx c^\dagger(x) H_0(x) c(x) + \frac{1}{2} \int dx dx' c^\dagger(x) c^\dagger(x') W(x, x') c(x') c(x),
$$

(2.12)

where $\hat{H}_0$ contains the kinetic energy and electron-nucleus attraction (external po-
tentials can also be included in this operator). In this work, the two-body interaction
$\hat{W}$ will be the Coulomb interaction. In this thesis, we adopt atomic units, where the
reduced Planck constant $\hbar = 1$ and Bohr’s radius $a_0 = 1$. An outline of the most
important definitions in this system is given in App. A. In coordinate-time space,
the Green’s function is defined as [2]:
\[
G(x, t; x', t') = -i \left\langle 0(A) \left| T[c_H(x, t)c_H^\dagger(x', t')] \right| 0(A) \right\rangle / \left\langle 0(A) \left| 0(A) \right\rangle \right.
\] (2.13)
The physical ground state of the \( A \)-particle system is denoted by \( |0(A)\rangle \) and \( c_H(x, t) \) [\( c_H^\dagger(x, t) \)] is the Heisenberg annihilation (creation) operator, which creates a hole (particle) at space-time coordinate \((x, t)\). Note that in the case of an interacting many-body system, the ground state \( |0(A)\rangle \) can no longer be described by a simple Slater determinant as for a noninteracting system. The single-particle propagator involves the time-ordering operator \( T \), which rearranges the Heisenberg operators according to the time coordinate: an operator involving a larger time coordinate is placed to the left of one involving a smaller time. In the case of fermionic operators, the anti-commutation relations generate a factor \((-1)\) for each permutation, i.e. depending on the number of interchanges needed to arrive at the correct time order, an overall minus minus sign may appear. Writing out the time-ordering operator explicitly, we arrive at [assuming \( |0(A)\rangle \) to be normalized to 1]
\[
G(x, t; x', t') = -i \left\langle 0(A) \left| c_H(x, t)c_H^\dagger(x', t') \right| 0(A) \right\rangle \theta(t - t') + i \left\langle 0(A) \left| c_H^\dagger(x', t')c_H(x, t) \right| 0(A) \right\rangle \theta(t' - t).
\] (2.14)
The definition of the Green’s function is now intuitively obvious. If \( t > t' \), the Green’s function describes a particle on top of the ground state of the \( A \)-body system, propagating from its point of creation at space-time coordinate \((x', t')\) to its annihilation at \((x, t)\), where the system returns to the ground state \(|0(A)\rangle\). During this propagation, the particle interacts with the rest of the many-body system as is clear from the time evolution of the Heisenberg operators \( c_H(x, t) = e^{iHt}c(x)e^{-iHt} \) [where \( c(x) \) is the corresponding operator in the Schrödinger picture]. An analogous explanation follows when \( t' > t \): the Green’s function then describes the propagation of a hole in the \( A \)-particle system. Stated briefly, by means of the Green’s function, we can follow the propagation of a particle or a hole through the system.

![Figure 2.1: Antisymmetrization of the two-body Coulomb interaction.](image)

Similar to the situation of a system with only one particle, a Fourier transformation from coordinate-space-time domain to configuration-energy space can be
performed (we again assume that the Hamiltonian is time independent such that the Green’s function only depends on the time difference \( t - t' \)). The second-quantization form of the Hamiltonian in configuration space reads

\[
\hat{H} = \hat{H}_0 + \hat{W} = \sum_{\alpha, \beta} \langle \alpha \mid H_0 \mid \beta \rangle c^\dagger_\alpha c_\beta + \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} \langle \alpha \beta \mid W \mid \gamma \delta \rangle_{\alpha \beta} c^\dagger_\alpha c^\dagger_\beta c_\gamma c_\delta,
\]

where the matrix element of the Coulomb interaction is antisymmetrized \( \langle \alpha \beta \mid W \mid \gamma \delta \rangle_{\alpha \beta} = \langle \alpha \beta \mid W \mid \gamma \delta \rangle - \langle \alpha \beta \mid W \mid \delta \gamma \rangle \), see Fig. 2.1). As in section 2.2, the labels \( \alpha, \beta, \ldots \) denote the quantum numbers of the single-particle (s.p.) states in a complete orthonormal basis set.

The Green’s function is cast into the form

\[
G_{\alpha \beta}(E) = \langle 0(A) \mid c_\alpha \frac{1}{E - H + E_{0(A)} + i\eta} c^\dagger_\beta + c^\dagger_\beta \frac{1}{E - H - E_{0(A)} - i\eta} c_\alpha \mid 0(A) \rangle,
\]

with a similar interpretation for the two distinct terms as in coordinate-time space given above. The creation operator \( c^\dagger_\alpha \) is related to its space-time counterpart by \( c^\dagger(x) = \sum_\alpha \phi^*_\alpha(x) c^\dagger_\alpha \), where \( \phi_\alpha(x) \) is the orbital in the complete set of states that corresponds to the label \( \alpha \). An analogous expression holds for the annihilation operator \( c_\alpha \). Note that the form (2.16) of the s.p. propagator in an interacting many-body system is alike to Eq. (2.7), except that in the latter case, of course, we only have the term corresponding to a particle propagating on top of the vacuum state.

From Eq. (2.16), an alternative expression of the Green’s function is derived by inserting a complete set of orthonormal states of the \( (A + 1) \)- and \( (A - 1) \)-particle system:

\[
\sum_{N(A+1)} | N(A+1) \rangle \langle N(A+1) | = 1, \quad \sum_{N(A-1)} | N(A-1) \rangle \langle N(A-1) | = 1,
\]

and we arrive at the so-called **Lehmann representation** for the Green’s function

\[
G_{\alpha \beta}(E) = \sum_{N(A+1)} \frac{\langle 0(A) \mid c_\alpha \mid N(A+1) \rangle \langle N(A+1) \mid c^\dagger_\beta \mid 0(A) \rangle}{E - E_{N(A+1)} + E_{0(A)} + i\eta} + \sum_{N(A-1)} \frac{\langle 0(A) \mid c^\dagger_\beta \mid N(A-1) \rangle \langle N(A-1) \mid c_\alpha \mid 0(A) \rangle}{E + E_{N(A-1)} - E_{0(A)} - i\eta}.
\]

The sum over the \( (A \pm 1) \) energy states also includes an integration part over the continuum orbitals in the spectrum. From the Lehmann representation, it is clear that the Green’s function describing a particle (or hole) in an \( A \)-body system has the
form of a weighted average of properties of the \((A \pm 1)\)-particle system, consistent
with the “propagator interpretation” of Eq. (2.14) involving particles or holes on
top of the \(A\)-particle ground state.

The Lehmann representation of the Green’s function involves important observ-
able values some of which are accessible in experiment. The location of the poles of the
Green’s function is determined by the eigenenergies \(E_{N(A \pm 1)}\) of the eigenstates in
the \((A \pm 1)\)-electron system, relative to the ground-state energy of the \(A\)-electron
atom, \(E_0(A) - E_{N(A \pm 1)}\) or \(E_{N(A-1)} - E_0(A)\). The discrete bound states of the
\((A \pm 1)\) states give rise to simple poles in the Green’s function, while continuum
states form a left-hand and right-hand branch cut (see Fig. 2.2). We observe that,
due to the so-called particle-hole gap in normal finite Fermi systems, there is no
overlap between the regions of the \((A-1)\) and the \((A+1)\) poles. Two of these poles

\[
\text{Im}\{E\} \\
\text{Re}\{E\}
\]

\(E_0(A-1)\)

\(E_0(A+1)\)

\(E_0(A)\)

Figure 2.2: Pole structure of the Green’s function.

are of special interest, namely those where only differences between ground states
are considered: the electron affinity can be defined as (cf. [12]) \(\mathcal{A} = E_0(A) - E_{0(A+1)}\)
and the first ionization potential as \(I = E_{0(A-1)} - E_0(A)\).

Also, the residues at the poles are related to the corresponding Feynman-Dyson
amplitudes [8] \(\langle N(A-1) \mid c_\alpha \mid 0(A) \rangle\) and \(\langle 0(A) \mid c_\alpha \mid N(A+1) \rangle\). The square of
the \(N(A-1)\) amplitude can be measured in \((e,2e)\) experiments, where an electron
is scattered on an atomic target with a sufficiently high energy to knock out one of
the electrons of the atom (see experimental results in chapters 3 and 4). The sum
of the squares of these amplitudes leads to an important experimental observable
namely the spectroscopic factor:

\[
S^p_{N(A+1)} = \sum_\alpha |\langle 0(A) \mid c_\alpha \mid N(A+1) \rangle|^2,
\]

\[
S^h_{N(A-1)} = \sum_\alpha |\langle 0(A) \mid c_\alpha^\dagger \mid N(A-1) \rangle|^2.
\] (2.19)
We also want to mention for future use, the particle spectral function

\[ S_\alpha^p (E) = \sum_{N(A+1)} | \langle 0(A) | c_\alpha | N(A+1) \rangle |^2 \delta \left( E - E_{N(A+1)} + E_0(A) \right), \]  

(2.20)

and the hole spectral function:

\[ S_\alpha^h (E) = \sum_{N(A-1)} | \langle 0(A) | c_\alpha^\dagger | N(A-1) \rangle |^2 \delta \left( E + E_{N(A-1)} - E_0(A) \right). \]  

(2.21)

The spectral functions are related to the first, respectively second term of Eq. (2.18) by means of the identity

\[ \frac{1}{x \pm i\eta} = P_v \left( \frac{1}{x} \right) \mp \pi i \delta(x), \]

(2.22)

where \( P_v \) stands for the principal value. The physical interpretation of the spectral function is the probability to remove or add a particle from or to the \( A \)-particle correlated ground state and leave the resulting system in a state with energy \( E \).

Finally, we illustrate the statement made in the introduction that we can determine all single-particle properties of a many-body system, once the single-particle Green’s function has been calculated.

If we consider any one-body operator \( \hat{O}^{(1)} \) in second quantization:

\[ \hat{O}^{(1)} = \sum_{\alpha \beta} \langle \alpha | O | \beta \rangle c_\alpha^\dagger c_\beta, \]

(2.23)

we see from Eq. (2.18) that the correlated ground-state expectation value of this operator can be found in terms of the s.p. propagator:

\[ \langle 0(A) | \hat{O}^{(1)} | 0(A) \rangle = \sum_{\alpha \beta} \langle \alpha | O | \beta \rangle \langle 0(A) | c_\alpha^\dagger c_\beta | 0(A) \rangle \]

\[ = \sum_{\alpha \beta} \langle \alpha | O | \beta \rangle \int_{-\infty}^{\infty} \frac{dE}{2\pi i} e^{i\zeta E} G_{\beta\alpha}(E), \]

(2.24)

where the factor \( e^{i\zeta E}(\zeta > 0) \) ensures that only the backward part of the Green’s function [the second term in Eq. (2.18)] is selected. A special example is the one-particle density. By definition, we have

\[ \hat{\rho} = \sum_\alpha c_\alpha^\dagger c_\alpha. \]

(2.25)

Using Eq. (2.24), we find

\[ \langle 0(A) | \hat{\rho} | 0(A) \rangle = \sum_{\alpha \beta} \langle \alpha | \delta_{\alpha\beta} | \beta \rangle \int_{-\infty}^{\infty} \frac{dE}{2\pi i} e^{i\zeta E} G_{\beta\alpha}(E) \]

\[ = \sum_\alpha \int_{-\infty}^{\infty} \frac{dE}{2\pi i} e^{i\zeta E} G_{\alpha\alpha}(E). \]

(2.26)
In this way, we indeed see that knowledge of the s.p. Green’s function leads to the s.p. density. In general, expectation values of a two-body operator with respect to the exact ground state would require a two-particle Green’s function. However, as we will see in the next chapter, for the special case of the total energy we can use the s.p. propagator as well.

The merit of the Green’s function for a many-particle study is now obvious. In the next section, it will be shown how the s.p. propagator can be determined.

2.4 The Dyson equation for the Green’s function.

It was already noted in the introduction that the Green’s function formalism is founded on a perturbative basis: a perturbation series of the Green’s function is performed in terms of the residual two-body Coulomb interaction. It has become customary to use Feynman diagrams when dealing with perturbation calculus as an efficient way to represent different terms in the series. A very important property of Green’s function theory is that it is perfectly clear which Feynman diagrams are included in each order. It also distinguishes itself from more common perturbation schemes such as Rayleigh-Schrödinger by the fact that the perturbation series is constructed such that each order incorporates an infinite sum of related diagrams. The construction of a perturbation series for the s.p. Green’s function is based on the Gell-Mann and Low theorem. Without going into an in-depth analysis, we outline the use of this theorem, since the so-called adiabatic-connection method of Density Functional Theory (to be discussed in chapter 5) is based on the same ideas as this theorem. Details on the Gell-Mann and Low theorem can be found in e.g. [2] or [13].

As is common in a perturbation analysis, the complete Hamiltonian $H$ of the interacting many-body system is divided into a one-body part $H^{(0)}$ and a perturbation $H^{(1)}$, which will consist here of the two-body interaction solely. It is the purpose to construct a fictitious time-dependent problem, such that the two-body effects in $H^{(1)}$ are gradually integrated in the scheme. Therefore the following form is proposed for the exact Hamiltonian: $H_n(t) = H^{(0)} + H_n^{(1)}(t) = H^{(0)} + e^{-\eta t} H_n^{(1)}$ (with $\eta > 0$). This Hamiltonian coincides with $H^{(0)}$ at $t = \pm \infty$ and reaches the full Hamiltonian at $t = 0$: $H_n(0) = H$. As is well-known from standard quantum mechanics, the time evolution operator [where the subindex $I$ of the perturbation indicates that the operator is considered in the interaction picture: $H^{(1)}_I(t) = e^{iH^{(0)}t} H^{(1)} e^{-iH^{(0)}t}$]

$$U_\eta(t, t') = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_t^{t'} dt_1 \int_t^{t} dt_2 \cdots \int_t^{t_n} dt_n e^{-\eta [|t_1| + \cdots + |t_n|]}$$

$$\mathcal{T}[H^{(1)}_I(t_1) H^{(1)}_I(t_2) \cdots H^{(1)}_I(t_n)], \quad (2.27)$$
gives the evolution of an eigenfunction of $H_{\eta}(t)$ by

$$|\Psi_{\eta}(t)\rangle = U_{\eta}(t, -\infty) |\Phi\rangle,$$  \hspace{1cm} (2.28)

where the Slater determinant $|\Phi\rangle$ is an eigenfunction of $H^{(0)}$ \(\|\Phi_0\) will denote the ground state of $H^{(0)}$. The adiabatic factor $e^{-\eta[H]}$ was expressed explicitly in Eq. (2.27), such that the index $\eta$ in $H^{(1)}_{\eta}(t)$ could be discarded. On the other hand, an additional index was introduced to stress the dependence of the wave function and time-evolution operator on the parameter $\eta$. It is the expectation that if $\eta$ is infinitesimally small, i.e. the residual interaction is turned on adiabatically, the ground state has time to adjust to the potential. Therefore it is acceptable to suppose that the ground state $|\Phi_0\rangle$ of the uncorrelated system $[H^{(0)}]$ will evolve towards the ground state $|\Psi_{\eta}(0)\rangle$ of the fully interacting system $[H_{\eta}(0)]$. The question is whether we can find the ground state $|0(A)\rangle$ of the physical system by taking the limit:

$$|0(A)\rangle = |\Psi_{\eta}(0)\rangle = \lim_{\eta \to 0} |\Psi_{\eta}(0)\rangle.$$ \hspace{1cm} (2.29)

The circumstances for which this limit yields physical results are given by the Gell-Mann and Low theorem [14], which states:

1. If the quantity $\lim_{\eta \to 0} \frac{U_{\eta}(0, -\infty) |\Phi_{\eta}\rangle}{\langle \Phi_{\eta} | \Psi_{\eta}(0)\rangle}$ exists to all orders in perturbation theory, then it is an exact eigenstate of $H \|\Phi_0\rangle$ is the ground state of $H^{(0)}$, i.e. the uncorrelated ground state, but the theorem does not guarantee that the evolved state is the ground state of $H^{(1)}$.

2. The limit $\lim_{\eta \to 0} |\Psi_{\eta}(0)\rangle$ does not exist, since $|\Psi_{\eta}(0)\rangle \sim e^{-\frac{f(\lambda)}{\eta}}$ as $\eta \to 0$ under the conditions in (1) \(f(\lambda)\) is a function of the coupling constant $\lambda$ used to determine the order in our perturbation calculus.

It is obvious that the infinite phase appearing in (2) will cancel with the denominator in (1). Note that the theorem does not provide us with strict conditions under which the limit $\eta \to 0$ exists. The value of the theorem is only that it ensures us that we arrive at an exact, well-defined eigenstate of the full hamiltonian if we can calculate the limit $\eta \to 0$ from perturbation theory.

Also, the following identity can be shown to hold:

$$\langle \Phi_0 | \mathcal{T}[O_{H}(t)O_{H}(t')]| \Psi_0 \rangle = \lim_{n \to 0} \frac{1}{\langle \Phi_0 | U_{\eta}(\infty, -\infty) | \Phi_0 \rangle} \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{\infty} dt_1 \ldots \int_{-\infty}^{\infty} dt_n e^{-\eta(|t_1|+\ldots+|t_n|)} \mathcal{T}[H_{\eta}^{(1)}(t_1) \ldots H_{\eta}^{(1)}(t_n) O_{t}(t) O_{t}(t')]| \Phi_0 \rangle.$$ \hspace{1cm} (2.30)
Applied to the definition of the Green’s function Eq. (2.13), we find in configuration-time space the important representation of the single-particle Green’s function

\[
iG_{\alpha\beta}(t, t') = \lim_{\eta \to 0} \frac{1}{\eta [U_\eta(\infty, -\infty)]} \langle \Phi_0 | \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{\infty} dt_1 \ldots \int_{-\infty}^{\infty} dt_n \exp[-i(t-t_1)H^{(1)}(t_1) + \ldots + i(t-t_n)H^{(1)}(t_n)] \rangle | \Phi_0 \rangle.
\]

This form is well suited to perform a diagrammatic analysis of the perturbation series for the single-particle propagator. After expanding the two-body perturbation term

\[
H^{(1)}_i(t) = \frac{1}{4} \sum_{\alpha \beta \gamma \delta} \langle \alpha \beta | H^{(1)} | \gamma \delta \rangle_{as} c^\dagger_{\alpha i}(t)c^\dagger_{\beta i}(t)c_{\gamma i}(t)c_{\delta i}(t),
\]

expression (2.31) involves time-ordered products of creation and annihilation operators. These products can be evaluated most elegantly by means of Wick’s theorem, which is outlined below.

Before starting the diagrammatic study and the discussion of Wick’s theorem, we first introduce some relevant definitions. Apart from the time-ordering operator, we can also introduce the normal-ordering operator \( \mathcal{N} \), defined with respect to the ground state \( | \Phi_0 \rangle \) of the noninteracting system associated with \( H^{(0)} \). This operator places in a product of annihilation and creation operators the annihilation operator of a particle (or creation operator of a hole) to the right of the creation operator of a particle (annihilation operator of a hole state). During the normal-ordering process, we treat all fermion-operators as if they anticommute. As a consequence of the definition of \( \mathcal{N} \), the expectation value of a normal-ordered product in the ground state of the noninteracting system always vanishes.

The time-ordering and normal-ordering operators give rise to the notion of the contraction of operators:

\[
c_{\alpha i}(t)c^\dagger_{\beta i}(t') = \langle \Phi_0 | T[c_{\alpha i}(t)c^\dagger_{\beta i}(t')] - \mathcal{N}[c_{\alpha i}(t)c^\dagger_{\beta i}(t')] | \Phi_0 \rangle.
\]

The quantum labels \( \alpha, \beta, \ldots \) specify a quantum state within the noninteracting system corresponding to \( | \Phi_0 \rangle \) in a unique way. We see that the Green’s function of the noninteracting system can be related to the contraction:

\[
iG^{(0)}_{\alpha\beta}(t, t') = c_{\alpha i}(t)c^\dagger_{\beta i}(t').
\]

Concerning nomenclature, we note that the Green’s function of the noninteracting system is also called the free s.p. propagator or the free s.p. Green’s function. In
the following, we will see how the Green's function of an interacting many-body system can be derived by means of perturbation theory from the free propagator. The Green's function of the interacting system will be referred to as the dressed or the true propagator. Writing out Eq. (2.34) explicitly, we have

\[
    c_\alpha(t)c_\beta^\dagger(t') = \begin{cases} 
        \delta_{\alpha\beta}e^{-i\epsilon_\alpha(t-t')} & t > t', \text{if } \alpha \text{ is a particle state} \\
        -\delta_{\alpha\beta}e^{-i\epsilon_\alpha(t-t')} & t < t', \text{if } \alpha \text{ is a hole state} \\
        0, & \text{otherwise.}
    \end{cases}
\] (2.35)

We note that the contraction is just a function of time (no operator) and that the absence of two-body correlations in \( \Phi_0 \) implies that the contraction is diagonal within the adopted basis of the noninteracting system. Also, it is clear that for the free single-particle Green's function \( G^{(0)}_{\alpha\beta}(t,t') \), the Heisenberg and interaction picture coincide: the time evolution of the creation- and annihilation operators in Eq. (2.34) entails a (pure) phase factor that involves only \( \epsilon_\alpha \), i.e. the single-particle energy of the state \( \alpha \) in the uncorrelated ground state.

To evaluate the expectation value of the time-ordering operator in the noninteracting ground state [see expansion of the Green's function Eq. (2.31)], Wick's theorem is applied. It states that in the evaluation of the terms in the expansion, only matrix elements are to be retained in which all operators are contracted pairwisely: depending on each contraction individually, the terms either vanish or consist of a product of free propagators \( G^{(0)} \) [see Eq. (2.34)]. Therefore, we only have to find all possible products of free propagators combined with the appropriate interaction lines to get all possible terms that contribute to order \( n \) in the perturbation expansion of the fully interacting Green's function \( G \). A handsome diagrammatic approach to construct these terms is the technique of Feynman diagrams.

Let us have a look at the evaluation of the first-order contribution to the numerator of Eq. (2.31) in terms of Feynman diagrams (see App. B):

\[
    \lim_{\eta \to 0} \left\langle \Phi_0 \right| \mathcal{T}\left[ H^{(1)}_I(t_1) c_{\alpha I}(t) c_{\beta I}^\dagger(t') \right] \left| \Phi_0 \right\rangle = \frac{-i}{4} \lim_{\eta \to 0} \sum_{\gamma \delta \xi \zeta} \int_{-\infty}^{\infty} dt_1 e^{-\eta|t_1|} \left\langle \gamma \delta | H^{(1)} | \epsilon \xi \zeta \right\rangle \left\langle \Phi_0 \right| \mathcal{T}\left[ c_{\gamma I}(t_1) c_{\delta I}(t_1) c_{\xi I}(t_1) c_{\zeta I}^\dagger(t_1) c_{\alpha I}(t) c_{\beta I}^\dagger(t') \right] \left| \Phi_0 \right\rangle. \] (2.36)

First order means that in the diagram only one interaction line appears.

If the interaction is antisymmetrized (see Fig. 2.1), the numerator of Eq. (2.31) can generate only two diagrams consisting of one interaction line and three free propagator lines \( G^{(0)} \) [Eq. (2.35)], as represented in Fig. 2.3. In the figure, time goes forward in the upward direction and free propagators are represented by single-lined arrows. The two time arguments of the Green's function appear as end points of the propagator. We note that only particle propagation is shown. The corresponding
hole propagation can be found by changing the direction of the arrows (making use of the Feynman interpretation of hole states as particles propagating backward in time \([15]\)). Since we integrate over all intermediate time points \(t_1\), the interaction can take place at any time before, between, or after \(t\) and \(t'\).

It can be shown that diagrams generated by the numerator which are composed of two separate parts \([\text{unlinked}, \text{see Fig. 2.3 (a)}]\), are exactly cancelled by vacuum diagrams generated in the expansion of the denominator (\textit{linked-cluster theorem} \([16]\)).

This phenomenon is related to the cancellation of divergent phase factors mentioned in the theorem of Gell-Mann and Low. Because of the linked-cluster theorem, Eq. (2.31) reduces to linked diagrams of the numerator only (hence the subindex \(L\)):

\[
iG_{\alpha\beta}(t, t') = \lim_{\eta \to 0} \langle \Phi_0 | \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n e^{-\eta(|t_1| + \cdots + |t_n|)} \rangle
\]
\[ T[H_1^{(1)}(t_1) \ldots H_1^{(1)}(t_n) c_{\alpha \alpha}(t) c_{\beta \beta}^\dagger(t')] | \Phi_0 \rangle_L. \quad (2.37) \]

The first-order term \( G^{(1)} \) is displayed in Fig. 2.3 (b). Note that due to the anti-symmetry of the interaction, the so-called exchange diagram is also included in the diagram of this figure.

We are now in a position to derive the central equation in the Green’s function formalism. The \( n^{th} \) order term in the perturbation expansion of the Green’s function consists of all topologically distinct and linked diagrams with \( n \) interaction lines connecting \((2n + 1)\) free propagators. As an example, the diagrams contributing to the second-order term \( G^{(2)} \) are drawn in Fig. 2.4. It is clear from this figure and from Fig. 2.3 (b) that all diagrams in the perturbation series will be constructed with free propagator lines at beginning and ending point. This enables us to write the perturbation expression \( G = G^{(0)} + G^{(1)} + G^{(2)} + \ldots \) diagrammatically as in Fig. 2.5.

![Figure 2.5: Perturbation expansion of the Green’s function using the reducible self-energy.](image)

A double-lined propagator stands for the single-particle propagator of the fully interacting many-body system, while, as already indicated, a single line denotes the free propagator. In the figure, we also introduced the reducible self-energy \( \Sigma^R \), which collects all possible interactions between the particle (hole) described by the Green’s function and the medium in which it propagates. In analytical form, the Green’s function becomes

\[ G_{\alpha \beta}(t, t') = \delta_{\alpha \beta} G_{\alpha \beta}^{(0)}(t, t') + \int_{-\infty}^{\infty} dt'' \int_{-\infty}^{\infty} dt''' \sum_{\alpha' \beta'} \delta_{\alpha \alpha'} G_{\alpha \alpha'}^{(0)}(t, t'') \Sigma_{\alpha' \beta'}^{R}(t'', t''') \delta_{\beta' \beta} G_{\beta' \beta}^{(0)}(t''', t'). \quad (2.38) \]

We can transform this equation into a more elegant form by further regrouping the perturbation expansion of the single-particle propagator. It appears that the reducible self-energy involves two kinds of diagrams: diagrams that can be decomposed in lower-order diagrams by removing just one free propagator (reducible diagrams).
and diagrams that can not be decomposed in such a way (irreducible diagrams). As an example, we can take a look at Fig. 2.4: the first diagram is only a repetition of the first-order linked diagram and is reducible, but the other two are irreducible. We can now extract from the reducible self-energy the elementary, irreducible building blocks and introduce the irreducible self-energy $\Sigma$ (sometimes denoted as $\Sigma^\circ$).

\[
\begin{align*}
\text{Diagram 1} & = \text{Diagram 2} + \text{Diagram 3} + \ldots \\
\end{align*}
\]

Figure 2.6: The irreducible self-energy.

In terms of diagrams, the irreducible (or proper) self-energy $\Sigma_{\gamma\delta}$ is shown in Fig. 2.6, and the perturbation expansion of the Green’s function is displayed in Fig. 2.7, or analytically

\[
G_{\alpha\beta}(t, t') = \delta_{\alpha\beta} G_{\alpha\beta}^{(0)}(t, t') + \sum_{\alpha'\beta'} \int dt_1 dt_2 \delta_{\alpha\alpha'} G_{\alpha\alpha'}^{(0)}(t, t_1) \Sigma_{\alpha'\beta'}(t_1, t_2) \times \\
\left[ \delta_{\beta\gamma} G_{\beta\gamma}^{(0)}(t_2, t') + \sum_{\gamma\gamma'} \int dt_3 dt_4 \delta_{\gamma\gamma'} G_{\gamma\gamma'}^{(0)}(t_2, t_3) \Sigma_{\gamma\gamma'}(t_3, t_4) \times \ldots \right].
\]

(2.39)

It is clear that the correlated motion of a particle (hole) in a many-body system consists of a succession of free-particle motion and interaction with the medium.

From Fig. 2.7 or Eq. (2.39) the final form of the equation determining the Green’s function is derived: on the right-hand side of the equation, we can recognize the fully interacting propagator. We therefore rewrite Eq. (2.39) in a more concise form and arrive at Dyson’s equation:

\[
G_{\alpha\beta}(t, t') = \delta_{\alpha\beta} G_{\alpha\beta}^{(0)}(t, t') + \sum_{\alpha'\beta'} \int dt_1 dt_2 \delta_{\alpha\alpha'} G_{\alpha\alpha'}^{(0)}(t, t_1) \Sigma_{\alpha'\beta'}(t_1, t_2) G_{\beta\beta}(t_2, t').
\]

(2.40)

It is represented by means of diagrams in Fig. 2.8.

Similarly, the Dyson equation in configuration-energy space reads

\[
G_{\alpha\beta}(E) = \delta_{\alpha\beta} G_{\alpha\beta}^{(0)}(E) + \sum_{\alpha'\beta'} \delta_{\alpha\alpha'} G_{\alpha\alpha'}^{(0)}(E) \Sigma_{\alpha'\beta'}(E) G_{\beta\beta}(E),
\]

(2.41)
2.4. The Dyson equation for the Green's function.

which represents the Fourier transform of Eq. (2.40). We notice a striking resemblance with Eq. (2.11).

In most cases we will assume that the full Green’s function is diagonal in the basis used to represent configuration space. Then, it follows that the self-energy is diagonal as well, and, using the Fourier transform of Eq. (2.35), we can rewrite Eq. (2.41) as

$$G_{\alpha\alpha}(E) = \frac{1}{G_{\alpha\alpha}^{(0)}(E)^{-1} - \Sigma_{\alpha\alpha}(E)}.$$  \hspace{1cm} (2.42)

From this expression, it is noted that if we are able to find the exact form of the proper self-energy (the self-energy for short) in a physical system, the exact Green’s function of that system can be calculated and the many-body problem would be solved exactly. It is obviously impossible to find an exact expression for the self-energy and therefore we will have to derive acceptable approximations for the self-energy. These approximations can be found by considering the perturbation expansion of the self-energy (see Fig. 2.6) in terms of the two-body interaction and truncating at some appropriate order.

Another, more concise, way to represent the irreducible self-energy involves the concept of skeleton diagrams. These are diagrams that do not contain any (irreducible) self-energy insertions other than themselves. Some examples of skeleton and nonskeleton diagrams are displayed in Fig. 2.9.

The irreducible self-energy can now be reproduced by taking into account only these skeleton diagrams if we dress the diagrams, i.e. we replace in the self-energy every free propagator $G^{(0)}$ by the correlated Green’s function $G$. The irreducible self-energy can then be represented as in Fig. 2.10.
Figure 2.8: The Green’s function as determined by Dyson’s equation.

The general scheme to solve Dyson’s equation is now obvious. The first step is to truncate the self-energy (as represented in terms of dressed skeleton diagrams) at some order in the interaction. Since the truncated self-energy depends on the Green’s function we are looking for, the corresponding Dyson equation is to be solved self-consistently: first we make some initial guess for the Green’s function (e.g. the Green’s function of a suitable noninteracting system) and apply it in the evaluation of the truncated self-energy. In this way, a first-iteration estimate of the self-energy is obtained.

Figure 2.9: Skeleton and nonskeleton diagrams.

From the Dyson equation in the form of Eq. (2.42) we calculate an update for the Green’s function, from which a new estimate for the self-energy can be found. The requirement of a self-consistent solution increases the computational demand, but, since more diagrams are taken into account, it ensures that some basic conservation laws are obeyed (see next chapter). Also, because of the self-consistent approach, the final result is independent of the initial guess.

In this thesis, only first- and second-order contributions to the self-energy are
2.4. The Dyson equation for the Green’s function.

taken into consideration. If the bare Coulomb interaction is used in the diagrams, the first-order contribution to the self-energy is equivalent to the Hartree-Fock (HF) approximation (first diagram in Fig. 2.10). The Dyson equation becomes

$$G^{(1)}_{\alpha\alpha}(E) = \frac{1}{G^{(0)}_{\alpha\alpha}(E)^{-1} - \Sigma^{(1)}_{\alpha\alpha}(E)},$$  \hspace{1cm} (2.43)

where $G^{(0)}_{\alpha\alpha}(E)$ is the free-particle propagator. From the Feynman diagram for the first-order self-energy, we have

$$\Sigma^{(1)}_{\alpha\alpha}(E) = (-1) \frac{i}{2\pi} \sum_{\beta} \langle \alpha \beta | W | \alpha \beta \rangle_{\alpha\alpha} \int dE' e^{iE'E} G^{(1)}_{\beta\beta}(E'),$$  \hspace{1cm} (2.44)

where $W$ is the Coulomb interaction between the electrons in the system. This equation indicates that $\Sigma^{(1)}_{\alpha\alpha}(E)$ is in fact energy independent (note that we only consider two-body interactions that are energy independent), which entails a large computational advantage next to the situation where higher-order terms are included. However, if we project the HF potential to coordinate space, the exchange (Fock) term introduces a nonlocality that will require special attention when the HF equations are solved (see next chapter).

$$
\begin{align*}
&\begin{array}{c}
\begin{array}{c}
\text{Figure 2.10: Skeleton expansion for the irreducible self-energy.}
\end{array}
\end{array}\\
&\begin{array}{c}
\begin{array}{c}
\text{Due to the energy independence, the self-energy assumes merely the role of an external field acting on the particle (or hole) described by the Green’s function. This means that in the first-order approximation of a many-body system, the interaction between the particles is averaged out completely (in fact, the first-order self-energy represents the mean field, i.e. the average influence of all the other particles in the system). As already indicated, the Green’s function of a noninteracting system assumes a simple form:}
\end{array}
\end{array}\\
&\begin{array}{c}
\begin{array}{c}
G^{(1)}_{\alpha\alpha}(E) = \frac{\theta(E - \epsilon_{\alpha}^{HF} - \epsilon_{F})}{E - \epsilon_{\alpha}^{HF} + i\eta} + \frac{\theta(\epsilon_{F} - \epsilon_{\alpha}^{HF})}{E - \epsilon_{\alpha}^{HF} - i\eta},
\end{array}
\end{array}
\end{align*}
$$
of the highest occupied and the lowest unoccupied HF state \[ \varepsilon_F = -\frac{1}{2}(\mathcal{I} + \mathcal{A}) \]. This means that the absolute value of the Fermi energy within Hartree-Fock is an approximation to the chemical potential \( \mu \). The expression (2.45) can be derived directly from the definition of the single-particle propagator or from Lehmann's representation (2.18).

When inserting this form of the Green's function in Eq. (2.44) we find (keeping in mind the fact that the infinitesimal parameter \( \zeta \) is positive and we therefore have to close the contour in the upper half plane when performing the integration)

\[
\Sigma^{(1)}_{\alpha\alpha} = \sum_\beta \langle \alpha\beta | W | \alpha\beta \rangle^{(\alpha\beta)} \theta(\varepsilon_F - \varepsilon^{HF}_\beta),
\]

(2.46)

which indeed is the expression for the HF mean field.

In the HF model, it is very easy to describe a many-body system: we simply have to fill all single-particle levels up to the Fermi level. Particles can only be added above the Fermi level and removed only below this level. Therefore, the spectral functions (2.20) and (2.21) consist of a single delta-function. When correlations beyond Hartree-Fock are added, this simple picture is no longer valid: the one-particle (one-hole) configuration mixes with more complex excitations and the spectral functions manifest more structure. To conclude this discussion of the first-order approximation, we note that a HF electron is a typical example of a \textit{quasi-particle}, which can be seen as the equivalent of a free particle in a many-body medium. In general, a quasi-particle behaves as a real particle but the other particles influence its movement and \textit{vice versa} (which can lead \textit{e.g.} to a screening of the interaction in the system). Consequently, the "bare" particle is "dressed" by the interaction with the medium: its dispersion relation is altered compared to that for a free particle but it still has a relatively high life time. As an example, in the Hartree-Fock approximation, the electron drags an exchange hole with it, which represents the area where the particle affects other electrons. The special thing about a HF quasi-particle is that its life time is infinite, just as for a free electron. In chapter 6, we will provide a more rigorous discussion of the quasi-particle concept.

The second-order self-energy is, contrary to the first-order case, energy dependent, which is a manifestation of the fact that the two-body degrees of freedom are being folded into the one-body picture of the single-particle propagator. It plays the role of a generalized mean field felt by an electron moving with energy \( E \) in the global electron system. This energy dependence is equivalent to introducing collisions (interactions) between the particles, leading to excitations with a finite life time. Contrary to Hartree-Fock, where the particles move as quasi-particles, the collective features in the second-order term make the electrons move more like a cloud rather than as individual particles. Yet, even in second order, there are quasi-particles near the Fermi energy of the system. In fact, it has been proven that in any many-particle system for which perturbation theory converges, there are
2.4. The Dyson equation for the Green’s function.

quasi-particles in the vicinity of the chemical potential $\mu$ [17]. Note that one way to describe the influence of the cloud around a particle phenomenologically is to introduce an effective mass for the electron. Therefore, the self-energy is sometimes called the mass operator.

The second-order contribution to the self-energy is represented in the second diagram of Fig. 2.10, and reads, according to the Feynman rules (see App. B),

$$\Sigma_{\alpha\alpha}(E) = \frac{1}{2\hbar^2} \sum_{\beta_1\beta_2\beta_3} \frac{1}{2} \left| \langle \alpha \beta_3 | W | \beta_1 \beta_2 \rangle_{\alpha\beta} \right|^2 \int dE_1 \int dE_2 G^{(2)}_{\beta_1\beta_1}(E - E_1 + E_2) G^{(2)}_{\beta_2\beta_2}(E_1) G^{(2)}_{\beta_3\beta_3}(E_2).$$

(2.47)

The additional factor $\frac{1}{2}$ is added to prevent double counting of diagrams, generated by the two equivalent fermion (particle) lines in the diagram for the second-order self-energy.

In a typical second-order calculation, the HF approximation is used as a starting point instead of the free propagator $G^{(0)}$:

$$G^{(2)}_{\alpha\alpha}(E) = \frac{1}{G^{(0)}_{\alpha\alpha}(E)^{-1} - \Sigma^{(1)}_{\alpha\alpha} - \Sigma^{(2)}_{\alpha\alpha}(E)}$$

$$= \frac{1}{G^{(1)}_{\alpha\alpha}(E)^{-1} - \Sigma^{(2)}_{\alpha\alpha}(E)}$$

$$= \frac{1}{E - \epsilon^{HF}_{\alpha} - \Sigma^{(2)}_{\alpha\alpha}(E)}.$$

(2.48)

The form of both second-order Green’s function and self-energy will be further developed in the next chapter.
Chapter 3

Self-consistent solution of Dyson’s equation: closed-shell atoms.

3.1 Introduction.

In this chapter, it will be discussed how Dyson’s equation for the Green’s function can be solved self-consistently up to second-order in the interaction, i.e. the skeleton self-energy series is truncated at second order. As indicated in the introduction to the previous chapter, the evaluation of the Green’s function can be very time consuming even when truncating at second order. We therefore restrict the study to atomic systems. Initially, we only consider closed-shell atoms, the extension to the open-shell case will be discussed in the next chapter. For these systems, we will find out how the propagator behaves in electron systems. Subsequently, this study will be used to assess the quality of the description of the same systems by means of Density Functional Theory.

It was indicated at the end of the previous chapter that prior to the second-order scheme, a Hartree-Fock (HF) calculation is performed. The first-order scheme is solved in coordinate-energy space, i.e. the HF equations, which represent a set of coupled integro-differential equations in coordinate space, are solved in an iterative way on a spatial grid, without the use of basis-set functions (e.g. Slater- or Gaussian-type orbitals). The advantage of this approach is that the asymptotic limits (close to the nucleus and very far from it) are described correctly, while the description of the cusp and asymptotic tail by for instance Gaussian basis functions is known to be erroneous. The second-order scheme, on the other hand, is solved in a (quasi-)complete and discrete basis set, which is obtained in a HF-like procedure. We chose to solve the Dyson equation in a self-consistent way (in the terminology of

Chapter 2: the skeleton diagrams are dressed, i.e. the self-energy is evaluated with the Green's function we are actually looking for. This approach has the advantage that the outcome of the procedure is independent of the initial estimate that was made to start the scheme and that some basic conservation rules are obeyed in the sense of Kadanoff-Baym [4], i.e. applying an infinitesimal disturbance on the system does not cause the values of the observables as predicted by the scheme to be altered (e.g. the number of particles in the system). One of the negative aspects of insisting on self-consistency is that, using a discrete basis set, the number of poles of the Green's function and self-energy increases tremendously over the iterations. To cope with this phenomenon, we made use of the BAGEL (BAsis GEnerated by the Lanczos algorithm) technique, which will be discussed in this chapter as well. Finally, some results as obtained for the closed-shell atoms He, Be, Ne, Mg, Ar, and Kr will be compared with other computational schemes and experiment. For the krypton atom, it may be necessary to include relativistic effects and also to consider the impact of screening on the single-particle (s.p.) properties. Both corrections are out of the scope of this work.

As an introduction, it is suitable to give a survey of studies that were already performed on the subject. Many attempts have been made to solve Dyson's equation up to orders beyond Hartree-Fock (see refs. [19]-[35]), but the calculations were never performed self-consistently. As discussed in the previous chapter, an obvious way of obtaining an approximation for the self-energy is to employ a finite expansion. One example of this method is the well-known outer-valence Green's function method (OVGF) [7, 22], based on the third-order expansion for the self-energy, where higher-order contributions are included by a renormalization procedure. Similar methods within this framework of third-order schemes have been worked out [21, 30, 33, 34, 35], and, in particular, we mention the work of J. Schirmer, et al. [18] who succeeded in an algebraic diagrammatic construction (ADC) of perturbation expansions. This ADC scheme has been applied for the evaluation of one-electron properties such as affinities, ionization energies, ... with great success (see [40, 41] and references quoted therein). Holleboom et al. [37, 38] evaluated the one-body Green's function using a second-order approximation to the self-energy that is constructed by means of the HF Green's function, i.e. the self-energy is not determined self-consistently. More recently, Warston et al. [39] applied an all-order evaluation scheme for the self-energy based on the systematic use of Dyson's integral equation. Their approach is complete up to third order in perturbation theory and large classes of higher-order effects are included in the propagator when solving Dyson's equation. However, since this scheme is not implemented self-consistently, it can not allow for the inclusion of infinite series of classes of diagrams.

All these schemes suffer from problems concerning the conservation of number of particles due to the lack of self-consistency. Scaling methods [40]-[43] have been suggested, but the physical justification of this correction is doubtful. In addition, all
3.2 Numerical solution of the HF equations in coordinate-energy space.

The HF equations in coordinate space read as:

\[
\left\{ -\frac{1}{2} \nabla^2 - \frac{Z}{r} + V_H(r) \right\} \varphi_\alpha(r) - \left[ \hat{V}_F \varphi_\alpha \right](r) = \epsilon^H_\alpha \varphi_\alpha(r), \tag{3.1}
\]

where \( \alpha \) comprises all the quantum labels necessary to specify the HF orbital uniquely and \( Z \) is the atomic number (since we are dealing with neutral atoms, this is also the number of electrons). We recall that atomic units are used throughout this work. The wave function \( \varphi_\alpha(r) \) is normalized as \( \int_0^\infty d^3r \varphi_\alpha(r) \varphi_\alpha^*(r) = \delta_{\alpha \beta} \).

For closed-shell systems, we make use of the spherical symmetry. Hence the HF secular Eq. (3.1) reduces to the following radial equations

\[
\left\{ -\frac{1}{2} \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \frac{Z}{r} + V_H(r) \right\} P_{nl}(r) - \left[ \hat{V}_F P_{nl} \right](r) = \epsilon^H_{nl} P_{nl}(r), \tag{3.2}
\]

where \( n \) is the principal quantum number and \( l \) the orbital momentum. The quantum numbers corresponding to the \( z \)-components of the orbital angular momentum (\( \tilde{l}_z \)) and the spin (\( \tilde{s}_z \)) will be denoted by \( m_l \) and \( m_s \) respectively. The radial wave functions \( P_{nl}(r) \) are related to the wave functions \( \varphi_\alpha(r) \) by

\[
\varphi_\alpha(r) = \phi_{nla}(r) Y_{m_\alpha}^{l_s}(\Omega) \chi_{m_{sa}}(s),
\]

\[
= \frac{P_{nla}(r)}{r} Y_{m_\alpha}^{l_s}(\Omega) \chi_{m_{sa}}(s), \tag{3.3}
\]

where \( Y_{m_\alpha}^{l_s}(\Omega) \) is the spherical harmonic corresponding to the quantum labels \( (l_\alpha, m_{l_\alpha}) \) and \( \chi_{m_{sa}}(s) \) is the Pauli spinor. The Hartree potential can be cast in the following form

\[
V_H(r) = \sum_{n'l'l'\mu_l'\mu_s'(\text{occ.})} \sum_{s'} \int d^3r' \phi_{n'l'}(r')^2 |Y_{l_l'}^{\mu_l'}(\Omega')|^2 |\chi_{m_{s'}}(s')|^2 \frac{1}{|r-r'|},
\]

\[
= \sum_{n'l'} [2(2l'+1)] \frac{1}{r} \int_0^\infty dr' P_{n'l'}(r')^2 + \int_r^\infty dr' \frac{1}{r'} P_{n'l'}(r')^2. \tag{3.4}
\]
The action of the non-local Fock potential on the wave function \( \varphi_{\alpha}(\vec{r}) \) equals
\[
\left[ \hat{V}_F \varphi_{\alpha} \right] (r, \Omega, s) = \sum_{\alpha' \text{ (occ.)}} \sum_{\gamma' \neq \gamma} \int d^3 r' \frac{\varphi_{\alpha'}^\dagger(r', \Omega', s') \varphi_{\alpha'}(r', \Omega', s') \varphi_{\alpha}(r, \Omega, s)}{|\vec{r}' - \vec{r}|} , \tag{3.5}
\]
and becomes after eliminating angular and spin degrees of freedom
\[
\left[ \hat{V}_F P_{nl} \right](r) = \sum_s \int d\Omega \frac{1}{2l'+1} \sum_{m_l m_j} Y_{m_l}^* (\Omega) \chi_{m_j}^* (s) \left[ \frac{1}{2l''+1} \sum_{m_l m_j} Y_{m_l}^* (\Omega) \chi_{m_j}^* (s) \sum_{\gamma' \neq \gamma} \int d^3 r' \frac{P_{nl'}(r') P_{nl'}(r') P_{nl'}(r') P_{nl'}(r')}{|\vec{r}' - \vec{r}|} \right] . \tag{3.6}
\]

We stress that the above expressions are only valid for closed-shell atoms.
The following boundary conditions are applied on the HF equations
\[
P_{nl}(0) = 0, \quad P_{nl}(r \to \infty) \to 0. \tag{3.7}
\]

There exists a variety of techniques to solve these equations. The so-called analytic HF method as first developed by Roothaan [44] and later extended to multiconfigurations by Hinze and Roothaan in ref. [45] used a basis set of radial functions \( r^m e^{-\zeta r} \) (the Slater orbitals) to expand the eigenfunctions \( P_{nl}(r) \). The problem of solving the HF equations is then reduced to a matrix diagonalization within the chosen basis and to finding the correct expansion coefficients for the Slater orbitals. Of course, the accuracy of the results depends on the size and the choice of the basis set. In order to optimize the quality of the basis set without inflating the dimension of the basis, the exponent \( \zeta \) of the Slater orbital for each value of \( m \) can be optimized. This optimization procedure is referred to as exponent optimization. In this method, it is very difficult to predict some estimate of the error due to basis-set restrictions.

Therefore, methods have been developed to integrate the HF equations numerically, based on finite differences (see e.g. [46],[47], and [48]). In this approach, the eigenfunctions \( P_{nl}(r) \) are replaced by the values \( P_{nl,i} \ i = 1, \ldots, J \) such that \( P_{nl,i} \) is an approximation to \( P_{nl}(r_i) \) on a discrete set of grid points \( r_i \). Differential and integral operators can then be replaced by their finite-difference analogues. The error in the approximation is directly related to the step size \( h \) of the grid: \( P_{nl,i} = P_{nl}(r_i) + O(h^p) \), with \( p \) the order of the method. The technique we have
used to solve the HF equations belongs to this class and will now be further developed.

First of all, we need an accurate sampling scheme for the radial coordinate. On the one hand, it is a great advantage when the grid points are equally spaced. However, in regions where some higher-order derivative is large, we should have a more tight sampling than where the derivatives are close to zero. For an atomic system, we expect that mainly in the vicinity of the nucleus a narrow grid is preferable, rather than at larger ranges of $r$. Therefore, a transformation to the logarithmic variable is often used, because an equally sampled logarithmic grid gives rise to points in normal $r$ space that become gradually more distant as $r$ increases. We apply the following transformation: $r = c_0 e^{c_1 \rho}$, with boundaries for the logarithmic variable $0 \leq \rho \leq 1$ and $c_0 = r_{\text{min}}, c_1 = \ln \frac{r_{\text{max}}}{r_{\text{min}}}$, such that $r_{\text{min}} \leq r \leq r_{\text{max}}$. We used the values $r_{\text{min}} = 10^{-6}$ a.u. and $r_{\text{max}} = 50$ atomic units. The logarithmic grid is sampled in an equidistant way. Note that a transformation of the independent variable induces a first-order derivative to appear in the laplacian. Since this is numerically unfavorable, we also transform the dependent variable $P_{nl}(r)$: $Q_{nl}(\rho) = P_{nl}(r(\rho)) \left( \frac{r'(\rho)}{r(\rho)} \right)^2$, which entails

\[
\frac{d^2}{dr^2} P_{nl}(r) = \frac{1}{c_1^2 r^{3/2}} \frac{d^2}{d\rho^2} \left[ \frac{Q_{nl}(\rho)}{r(\rho)} \right] - \frac{c_1^2}{4} Q_{nl}(\rho).
\]

(3.8)

On a discretized, equally spaced grid with step $\Delta$, we get [36]

\[
\frac{d^2}{d\rho^2} Q_{nl}(\rho) \rightarrow \frac{1}{\Delta^2} \left[ Q_{nl}(\rho_{i+1}) - 2Q_{nl}(\rho_i) + Q_{nl}(\rho_{i-1}) \right].
\]

(3.9)

The Hartree potential Eq. (3.4) turns into:

\[
V_H(r_i) = \sum_{n'l'} 2(2l' + 1) \left[ \frac{1}{r_i} \int_0^{r_i} d\rho' c_1 r(\rho')^2 Q_{n'l'}(\rho')^2 + \int_{r_i}^1 d\rho' c_1 r(\rho') Q_{n'l'}(\rho')^2 \right]
\approx \sum_{n'l'} 2(2l' + 1) c_1 \Delta \left[ \frac{1}{r_i} \sum_{s} r(s)^2 Q_{n'l'}(s)^2 + \sum_{s=\text{mag}} s \sum_{s'=s} r(s') Q_{n'l'}(s')^2 \right]
\approx \sum_{n'l'} 2(2l' + 1) c_1 \Delta \left[ \frac{1}{r_i} \sum_{s} r(s)^2 Q_{n'l',s}^2 + \sum_{s=\text{mag}} r(s) Q_{n'l',s}^2 \right].
\]

(3.10)

We see that in the discretized grid, the kinetic-energy operator and Hartree field give rise to a tridiagonal matrix, where the nondiagonal elements are only generated by the kinetic-energy term. Therefore, we can rewrite the HF equations in a discretized form, separating the Fock term from the other terms:

\[
TX - FX = \epsilon X,
\]

(3.11)
where \( T \) is the tridiagonal matrix, grouping kinetic energy, interaction with the nucleus and Hartree potential. The exchange- or Fock-potential is denoted by \( F \), which reads (discarding the spin degrees of freedom):

\[
FX = [\hat{V}_F P_{\text{nl}}](r_i) = \sum_{n'l'(\text{occ.})} (2l' + 1) \sum_{L=0}^{\infty} \left( \begin{array}{ccc} l & l' & L \\ 0 & 0 & 0 \end{array} \right)^2 r_i^{L+1} Q_{n'l'}(\rho(r_i)) c_1 \\
\left[ \frac{1}{r_i^{L+1}} \int_0^{\rho(r_i)} d\rho' \ r(\rho')^{L+2} Q_{n'l'}(\rho') Q_{nl}(\rho') + \frac{1}{r_i^L} \int_0^{\rho(r_i)} d\rho' \ r(\rho')^{L-1} Q_{n'l'}(\rho') Q_{nl}(\rho') \right].
\]

\[
\approx \sum_{n'l'(\text{occ.})} (2l' + 1) \sum_{L=0}^{\infty} \left( \begin{array}{ccc} l & l' & L \\ 0 & 0 & 0 \end{array} \right)^2 r_i^{L+1} Q_{n'l';i} c_1 \Delta \\
\left[ \frac{1}{r_i^{L+1}} \sum_{s=1}^{s_n} r_i^{L+2} Q_{n'l';s} Q_{nl;s} + \frac{1}{r_i^L} \sum_{s=1}^{s_m} \frac{1}{r_i^{L-s}} Q_{n'l';s} Q_{nl;s} \right].
\]

(3.12)

Finally, \( X \) in Eq. (3.11) represents the single-particle (s.p.) wave function on the sampling grid \( r(\rho_i), i = 1, \ldots, I \) and \( \epsilon \) is the s.p. energy.

Note that both the Hartree and Fock potentials depend on the wave functions we are looking for. This implies that a self-consistent approach has to be adopted to solve the HF equations. That procedure consists of first making some initial guess for the HF wave functions (e.g. based on the hydrogenlike problem) and evaluating the Hartree and Fock potentials. Once these potentials are evaluated, we can solve the resulting equation as a regular eigenvalue problem (see below). The new solution can be used to update the Hartree and Fock terms, from which a new estimate of the wave functions can be found. This process is repeated until convergence is reached for the wave function and the corresponding eigenenergy.

We will now focus on how we can solve Eq. (3.11) of a given iteration, with the Hartree and Fock potentials evaluated with the wave functions of the previous iteration. The presence of the inhomogeneous Fock term poses some additional difficulties and therefore the HF equations are solved in two stages. First, only the eigenvalue problem

\[
TX = \epsilon X,
\]

is considered, which is just a homogeneous eigenvalue problem. To solve this, an interesting property of a sturmian sequence can be employed [49]. Let us consider a
3.2. Numerical solution of the HF equations in coordinate-energy space.


\[ T = \begin{bmatrix} a_1 & b_1 & 0 & 0 & \ldots & 0 & 0 \\ b_1 & a_2 & b_2 & 0 & \ldots & 0 & 0 \\ 0 & b_2 & a_3 & b_3 & \ldots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ 0 & \ldots & 0 & b_{N-2} & a_{N-1} & b_{N-1} \\ 0 & \ldots & 0 & 0 & b_{N-1} & a_N \end{bmatrix}. \] (3.14)

The secular equation of this matrix is given by \( \det(T - \lambda) = 0 \) (with \( \det \) the determinant operator). We can now consider the (principal) minors \( T_i \) of \( T \), and define a corresponding polynomial via \( P_i(\lambda) = \det(T_i - \lambda) \). Then, due to the tridiagonality of \( T \), a recurrence relation can be derived between \( P_{i+1}(\lambda) \), \( P_i(\lambda) \), and \( P_{i-1}(\lambda) \):

\[ P_{i+1}(\lambda) = (\lambda - a_{i+1})P_i(\lambda) - b_{i-1}^2P_{i-1}(\lambda), \quad 1 \leq i \leq N - 1, \] (3.15)

with \( P_0(\lambda) = 1 \) and \( P_1(\lambda) = \lambda - a_1 \) (we define \( b_0 = 0 \)). This sequence is called a Sturmian sequence, and it has the property that between two subsequent roots of \( P_i(\lambda) = 0 \) there lies one single root of \( P_{i+1}(\lambda) = 0 \) (except, of course, at the end points). By determining where the polynomial changes sign, the intervals where the eigenvalues are to be found can be located. However, to avoid numerical problems, the intervals with the eigenvalues were distinguished by counting the number of intervals in which

\[ \frac{P_{i+1}(\lambda)}{P_i(\lambda)} = D_{i+1}(\lambda) = (\lambda - a_{i+1}) - \frac{b_{i-1}^2}{D_i(\lambda)}, \quad 1 \leq i \leq N - 1, \] (3.16)

has a negative (or positive) sign. We can now see how the tridiagonal-matrix eigenvalues of Eq. (3.13) are found. Starting from some lower bound value, the energy axis is scanned using a fixed incremental step. For each fixed energy value \( \lambda_0 \), the number \( F(\lambda_0) \) of sign changes of \( D_i(\lambda_0) \) is determined for \( i = 1, \ldots, N - 1 \). Next, we use the following interesting property of a Sturmian sequence: \( F(\lambda_0) \) equals the number of roots of \( D_N(\lambda) = 0 \) below \( \lambda_0 \). From this property, we see that we can select the intervals in which a root of \( D_N(\lambda) = 0 \) is located by determining the values \( \lambda_{\text{min}} \) and \( \lambda_{\text{max}} \) which yield \( F(\lambda_{\text{max}}) = F(\lambda_{\text{min}}) + 1 \). To determine the root, the bisection procedure is applied between \( \lambda_{\text{min}} \) and \( \lambda_{\text{max}} \). This process is performed by scanning over the energy axis until all \( N \) roots of \( D_N(\lambda) = 0 \) [or equivalently \( P_N(\lambda) = 0 \)] are determined.

Once the problem (3.13) is solved, the Fock term can be added to the equation. To obtain convergence, this term should be taken special care of by means of a separate self-consistency loop. Therefore, we introduce a projection operator in Eq. (3.11):

\[ [T - \frac{(FX_n)(FX_n)^\dagger}{X_n^\dagger FX_n}]X_{n+1} = \epsilon X_{n+1}, \] (3.17)
where an additional index has been introduced to keep track of the iteration in the Fock self-consistency loop. This equation is completely equivalent to Eq. (3.11) if convergence is reached, as long as $X$ is not orthogonal to $FX$. The eigenvalues of Eq. (3.17) are solution of

$$X_n^T F X_n = (F X_n)^1 \frac{1}{T - \epsilon} (F X_n),$$

(3.18)

which of course demands for a numerical solution. The solution of this transcendental equation is visualized in Fig. 3.1.

![Graphical solution of transcendental equation (3.18).](image)

The poles of the right-hand side of Eq. (3.18) are determined by the eigenvalues of the operator $T$. Intersections between the left-hand side of Eq. (3.18) (independent of s.p. energy) and the right-hand side determine the approximate HF eigenvalues of Eq. (3.18). Depending on the sign of the left-hand side, the HF eigenvalue is lower or higher than the corresponding Hartree eigenvalue. Since the Fock operator is positive definite (just as the Hartree operator, see App. C), the left-hand side is always positive and all energies are pushed downwards.

Because the right-hand side of Eq. (3.18) is always increasing between the asymptotes, it is guaranteed that only one solution is found between two eigenvalues of
3.2. Numerical solution of the HF equations in coordinate-energy space.

Eq. (3.13). Once the s.p. energy \( \epsilon \) has been determined, the corresponding eigenfunction \( X \) can be found by backward substitution in Eq. (3.17).

At this point, the occupied HF eigenvalues are obtained (note that within the HF formalism, the occupied states are the only bound states for a neutral atom). However, unoccupied states are important as well because in the second-order self-energy, intermediary particle and hole propagators appear (see e.g. Fig. 2.4). Since we will solve the second-order equation in a basis of HF orbitals, this means that we have to solve the HF equations for the virtual orbitals too. It is clear that an exact treatment of the continuum states is prohibitive, so we are faced with the problem to find an accurate description of the virtual states. Therefore, we introduce the following discretization scheme: we add to the HF mean field a confining potential \( U_i(r) \) of parabolic shape, at a relatively large distance \( R \) from the atomic center (see Fig. 3.2)

\[
U_i(r) = C_i \theta(r - R_i)(r - R_i)^2,
\]

where we denote the step function by \( \theta(x) \). It turned out to be advantageous to include a wall with parameters differing per angular-momentum block, hence the additional subscript \( i \). Of course, the introduction of the potential wall does not violate the spherical symmetry of the problem. Also, it only contributes to the diagonal elements of the matrix, so it is taken into account quite easily. In section 3.5, it will be discussed how the wall parameters are determined.

![Figure 3.2: Addition of the wall \( U_i(r) \) to the Hartree-Fock mean field \( V_{mf}(r) \).](image)

The actual algorithm to tackle Dyson’s equation in first order consists of three distinct steps. First the HF mean field is determined by solving the genuine HF equations (i.e. HF without enclosing wall) in a self-consistent way but only for the bound states. In a second step, the HF mean field generated by the bound levels
is kept fixed, but the parabolic potential wall is added to the problem and this set of modified HF equations is solved for both bound and virtual states. Strictly speaking, the procedure of the second step is not self-consistent, since the HF mean field is kept fixed. There is only a self-consistent loop involved in the treatment of the Fock potential. In this second step, the number of wave functions taken into account must be restricted and thus the set of eigenfunctions is truncated. However, a sufficiently high number of “continuum” wave functions is retained to make the set complete for all practical purposes: the way in which we determined the optimum dimension of the set is explained in section 3.5 as well. At the end of the second step, we have a (quasi-) complete set of eigenstates of the HF hamiltonian which is modified by the potential wall. To remove the influence of the wall on eigenfunctions and eigenvalues, the HF self-consistency problem is solved anew, now without wall, for both occupied and unoccupied states, using the complete set of discrete states obtained in the second step as basis set. Of course, it was checked as a test for the completeness of the truncated basis set that the eigenvalues for the bound states are sufficiently close to the ones we found in the first step. The self-consistent solution of the HF equations of the third step in this algorithm (i.e. without wall) is referred to in the following as the Dyson(1) scheme. It amounts to a solution of the HF problem in configuration-energy space, rather than in coordinate-energy space as was the case in the first two steps. Occasionally the term “Dyson(1) scheme” is also used to cover the three steps of the first-order scheme, but it is clear from the context when this more general meaning is used. At the end of the procedure, we have a (quasi-) complete set of eigenstates of the genuine HF hamiltonian, which is subsequently kept fixed during the rest of the algorithm (i.e. the self-consistent solution of the second-order Dyson equation).

3.3 Numerical solution of the second-order Dyson equation.

The HF approximation is actually the first-order truncation of the self-energy expansion. Therefore, the scheme discussed above to solve the HF equations (more specifically the third step of the scheme) is referred to as the Dyson(1) scheme. Now we will consider what happens if the second-order term of the self-energy series is added to the problem [Dyson(2) scheme].

We assumed the s.p. propagator and self-energy to be diagonal in the HF basis constructed by the Dyson(1) scheme, i.e. mixing between shells is not included. Indeed, in the case of the atoms studied here, the energy separation between orbitals that might generate a nondiagonal contribution to the Green’s function is large enough to expect only a minor effect on the results. For two cases (He and Be) we have checked that the effect of including off-diagonal self-energy contributions is quite small, at least for the first iteration in the self-consistency scheme.
The assumption that the self-energy matrix is diagonal in the HF basis is in principle not necessary; without this assumption, however, the numerical effort increases substantially during the iteration process to convergence.

Within this diagonal and discrete representation, the Green’s function in Eq. (2.18) can be written as a sum of simple poles,

\[ G_a(E) = \sum_j \frac{S^f_{a,j}}{E - \epsilon_{a,j} + i\eta} + \sum_j \frac{S^b_{a,j}}{E - \epsilon_{a,j} - i\eta}, \]  

(3.20)

where the summation index \( j \) is restricted to the \((A \pm 1)\)-electron states that can be reached from the closed-shell atom by adding or removing an electron in orbital \( a \). Also, we have introduced the following shorthand notation: \( \epsilon^f_{a,j} = E_{j(A+1)} - E_{0(A)} \) and \( \epsilon^b_{a,j} = E_{0(A)} - E_{j(A-1)} \) for the forward, resp. backward s.p. energies. It is also useful to mention that in Eq. (2.18), \( \alpha \) stands for a set of four quantum numbers:

\[ \alpha = (n_a, l_a, m_{l_a}, m_{s_a}), \]  

(3.21)

while \( a \) in Eq. (3.20) only contains a subset: \( a = (n_a, l_a) \). In fact,

\[ G_a(E) = \frac{1}{2(2I_a + 1)} \sum_{m_{l_a}, m_{s_a}} G_{\alpha\alpha}(E). \]  

(3.22)

We recall that the first term in Eq. (3.20) corresponds to the so-called forward propagating part and describes excitations in the \((A + 1)\)-electron system, whereas the second term (backward propagating part) describes excitations in the \((A - 1)\)-electron system.

The second-order self-energy of Eq. (2.47) becomes

\[ \Sigma^{(2)}_a(E) = \sum_{b,c,d} \sum_{j,k,l} \sum_{4(2I_a + 1)} \left\{ \frac{S^f_{c,j} S^f_{d,k} S^b_{b,l}}{E - \left( \epsilon^f_{c,j} + \epsilon^f_{d,k} - \epsilon^b_{b,l} \right) + i\eta} + \frac{S^b_{c,j} S^b_{d,k} S^f_{b,l}}{E - \left( \epsilon^b_{c,j} + \epsilon^b_{d,k} - \epsilon^f_{b,l} \right) - i\eta} \right\}, \]  

(3.23)

where

\[ F_{ab,cd} = \sum_{LS} (2L + 1)(2S + 1) \left| \langle (ab)LS \mid W \mid (cd)LS \rangle_{ab} \right|^2. \]  

(3.24)

As in the previous chapter, \( W \) denotes the two-body Coulomb interaction. Note that the continuum spectrum of poles of the Green’s function as displayed in Fig. 2.2, would lead eventually to a branch cut in the self-energy as well. The discretization scheme, however, enables us to work in a discrete framework over the whole spectrum.
We also recall that the diagonal form of the second-order Green’s function can be written as [Eq. (2.48)]

\[
G^{(2)}_a(E) = \frac{1}{E - \epsilon_a^{HF} - \Sigma^{(2)}_a(E)}.
\]  

(3.25)

For the self-consistent solution of Dyson’s equation we use the following iteration scheme. In the first iteration, the Green’s function of Eq. (3.20) is initialized with the HF approximation,

\[
G^{(2)[1]}_a(E) = \frac{\theta \left( \epsilon_f^{HF} - \epsilon_F \right)}{E - \epsilon_f^{HF} + i\eta} + \frac{\theta \left( \epsilon_F - \epsilon_f^{HF} \right)}{E - \epsilon_f^{HF} - i\eta}.
\]  

(3.26)

By means of Eq. (3.23), the second-order self-energy in the first iteration, \(\Sigma^{(2)[1]}_a\), can be found. Note that in the first iteration the \(S^J(S^0)\) coefficients are nonzero only for orbitals that are unoccupied (occupied) in the HF ground state. As a result, the summation in Eq. (3.23) is automatically restricted to intermediate states of two-particle one-hole and two-hole one-particle nature, as in standard perturbation theory [37].

In general, the second-order self-energy in the \(n\)th iteration, \(\Sigma^{(2)[n]}_a(E)\), is evaluated, through Eq. (3.23), with the \(n\)th iteration Green’s function \(G^{(2)[n]}_a(E)\). The Green’s function \(G^{(2)[n+1]}_a(E)\) of the next iteration is then given by

\[
G^{(2)[n+1]}_a(E) = \frac{1}{E - \epsilon_a^{HF[n]} - \Sigma^{(2)[n]}_a(E)}, \quad n = 1, 2, \ldots
\]  

(3.27)

In order to bring \(G^{(2)[n+1]}_a\) into the form of Eq. (3.20), the poles \(\epsilon_{a,j}^{[n+1]}\) of \(G^{(2)[n+1]}_a\) must be found. They are the solutions of

\[
\epsilon_{a,j}^{[n+1]} = \epsilon_a^{HF[n]} + \Sigma^{(2)[n]}_a \left( \epsilon_{a,j}^{[n+1]} \right),
\]  

(3.28)

and the corresponding residues \(S_{a,j}^{[n+1]}\) (the spectroscopic strength of the pole of the Green’s function) are, of course, given by

\[
S_{a,j}^{[n+1]} = \left( \frac{1}{1 - \frac{d}{dE} \Sigma^{(2)[n]}_a(E)} \right)_{E = \epsilon_{a,j}^{[n+1]}}.
\]  

(3.29)

The spectroscopic strength of an orbital is determined by the slope of the self-energy at the position of the pole (see also Fig. 3.4). If the slope is more negative, the pole contributes less to the Green’s function. Since the self-energy is monotonously decreasing between two of its poles, the residue is always less than or equal to one, becoming closer to zero if the self-energy is steeper at the intersection point. The
position of the pole $\epsilon_{a,j}^{[n+1]}$ relative to the Fermi energy determines whether it should be classified as a forward or a backward contribution to Eq. (3.20), i.e. $\epsilon_{a,j}^{[n+1]} > \epsilon_F$ indicates an $(A+1)$ excitation and $\epsilon_{a,j}^{[n+1]} < \epsilon_F$ an $(A-1)$ excitation.

As we discussed in the previous chapter, the self-energy series consists of dressed skeleton diagrams. This implies that the mean field $\Sigma^{(1)}$ also depends on the final (i.e., second-order) Green’s function. Hence, after each iteration the s.p. energies $\epsilon_a^{HF}$ in Eq. (3.27) are updated to reflect the changes in the occupations of all s.p. orbitals,

$$
\epsilon_a^{HF[n]} = \langle a \mid H_0 \mid a \rangle + \sum_{c,LS} \langle (ac)LS \mid W \mid (ac)LS \rangle_{as} \sum_j S_{c,j}^b[n].
$$

(3.30)

The above second-order algorithm is applied until convergence is reached. A diagrammatic summary is presented in Fig. 3.3.

![Diagram](image)

Figure 3.3: Diagrammatical representation of the second-order Dyson equation.

### 3.4 The BAGEL approximation.

#### 3.4.1 Introduction.

The main problem in the solution of the Dyson equation up to second order is the huge increase of the number of poles of Green’s function and self-energy over the iterations. This can be seen from Eq. (3.23) and the graphical solution of Eq. (3.28),
which is represented in Fig. 3.4 (where we considered the case of a particle state \( a \)). From this figure, it is clear that between two subsequent poles of the self-energy,

![Graphical solution of the transcendental equation (3.28).](image)

Figure 3.4: Graphical solution of the transcendental equation (3.28).

one pole of the Green’s function can be found. More specifically in the interval around the Fermi energy \( \epsilon_F \), we see that in iteration \( n+1 \), a pole \( \epsilon_{\alpha_1}^{(n+1)} \) arises with an energy which is lower than the HF energy due to correlations embedded in the second-order scheme. For a hole state, the HF pole would be pushed upwards in the self-energy configuration of Fig. 3.4.

It is also clear from Eq. (3.23) that for \( D \) poles of the Green’s function in iteration \( n \), about \( D^3 \) poles are generated for the self-energy, which leads to about \( D^3 (+1) \) poles for the Green’s function in iteration \( n + 1 \). The fact that there are more solutions to Eq. (3.28) than would be expected from the dimension of the basis set, is due to the nonlinearity of the eigenvalue equation introduced by the energy dependence of the self-energy.

To cope with this phenomenon, various approaches exist.

(i) In the one-pole approximation, the Green’s function is represented by only one pole, namely that one with the largest residue (therefore the method is also called the quasi-particle approximation). This approach is similar to the
HF concept, where the Green’s function is described using one pole, which
coincides with the HF s.p. energy. The main difference between the two
approaches is given by the residue or spectroscopic strength corresponding to the
single pole [see Eq. (3.20)]. In the HF approach, the strength is zero or unity,
depending on the particle occupancy of the orbital $\alpha$, while in the one-pole
approximation the interaction of the pure HF state with more complicated
states results into an admixture between these states. Due to this configura-
tion mixing, a strength differing from zero or unity is obtained. Physically,
this indicates that in the system, interactions (collisions) between the particles
are taken into account. Of course, the one-pole approach is not suited for a
detailed study of the Green’s function and it leads to a poor description of the
spectral function.

(ii) Another technique is the bin approximation (see e.g. [50, 51, 52]). In this
approach, the energy axis is divided in equal bins, the residues of all poles
that are located in the same bin are summed and the corresponding poles
inside that bin are presented by the center of the energy bin. This means that
for each iteration, a fixed number of poles and residues suffices to determine
the Green’s function and the self-energy. By choosing the bin width sufficiently
small, an accurate study can be made.

(iii) A more appropriate method to handle the huge number of poles is based on
the BAGEL scheme (BAsis GEnerated by the Lanczos algorithm, see refs. [52]
- [56]). In the following, we give an overview of the principles underlying this
approach.

To make the discussion of the BAGEL scheme more transparent, the second-
order self-energy is expressed in a more compact form as

$$\Sigma^{(2)}_{\alpha} (E) = \sum_{j=1}^{D_f} \frac{\sigma^f_j}{E - \omega^f_j + i\eta} + \sum_{j=1}^{D_b} \frac{\sigma^b_j}{E - \omega^b_j - i\eta},$$

(3.31)

and contains a large number $D_f + D_b$ of simple poles. In the so-called BAGEL($M,N$)
method, the number of poles is considerably reduced by choosing new poles and
residues which are determined in a judicious way

$$\tilde{\Sigma}^{(2)}_{\alpha} (E) = \sum_{j=1}^{M} \frac{\tilde{\sigma}^f_j}{E - \tilde{\omega}^f_j + i\eta} + \sum_{j=1}^{N} \frac{\tilde{\sigma}^b_j}{E - \tilde{\omega}^b_j - i\eta}.$$  

(3.32)

The new pole energies ($\tilde{\omega}^f_j$, $\tilde{\omega}^b_j$) and residues ($\tilde{\sigma}^f_j$, $\tilde{\sigma}^b_j$) are determined such that
the lowest energy-weighted moments of the distribution of self-energy strength are
reproduced. This means that for $p = 0, 1, \ldots, 2M - 1(2N - 1)$,
\[
\mu_a^f(p) = \sum_{j=1}^{D_f} \sigma_j^f (\omega_j^f)^p = \sum_{j=1}^{M} \tilde{\sigma}_j^f (\tilde{\omega}_j^f)^p
\]  \hspace{1cm} (3.33)

\[
\mu_a^b(p) = \sum_{j=1}^{D_b} \sigma_j^b (\omega_j^b)^p - \sum_{j=1}^{N} \tilde{\sigma}_j^b (\tilde{\omega}_j^b)^p.
\]  \hspace{1cm} (3.34)

To achieve the goal of this approach -the construction of these new pole energies and residues- the Lanczos algorithm is applied (see below). When limiting the number of forward poles to \(M\) and the number of backward poles to \(N\), we are dealing with the BAGEL(M,N) approximation for the self-energy \(\Sigma_a^{(2)}(E)\). As a consequence, it is clear that the resulting Green’s function will have the small number of only \(M + N + 1\) poles, and the dimensionality over successive iterations remains fixed. In the numerical applications we will keep \(M = N\), as for atomic systems there appeared to be no particular advantage in taking the number of forward poles \(M\) different from the number of backward poles \(N\). In the following subsections, the BAGEL approach will be discussed in detail. In subsection 3.4.2, we will show how the nonlinear eigenvalue problem (3.28), representing the Dyson equation, is transformed into a standard matrix eigenvalue equation. The matrix in this equation consists of a backward and a forward part related to the backward and forward part of the self-energy. By means of the Lanczos method (subsection 3.4.3), the matrix is transformed into a tridiagonal form. In subsection 3.4.4, it will be discussed how the Lanczos procedure can be applied such that the first-order moments \(0, \ldots, 2M - 1(2N - 1)\) of the forward and backward part of the self-energy are reproduced, in agreement with Eqs. (3.33)-(3.34). The tridiagonal matrix obtained by Lanczos is subsequently diagonalized, which gives the solution of Eq. (3.28); i.e. the poles of the Green’s function. The requirements (3.33-3.34) on the moments of the BAGEL self-energy \(\tilde{\Sigma}_a^{(2)}(E)\) also restrict the distribution of spectroscopic strength of the corresponding BAGEL Green’s function: its energy-weighted moments of order \(p = 0, 1, \ldots, 2P + 1\) (\(P = \min\{M, N\}\)) can be proven to equal the moments of the total spectroscopic distribution of the Green’s function that is obtained with the original self-energy \(\Sigma_a^{(2)}(E)\) (this will also be shown in subsection 3.4.4). In short, the BAGEL(M,N) approach reproduces the first \(2M\) (\(2N\)) order moments of the forward and backward part of the self-energy separately and reproduces the first \(2P + 2\) (\(P = \min\{M, N\}\)) order moments of the total spectroscopic distribution of the Green’s function.

It will become clear that the BAGEL method offers a tractable scheme to solve Dyson’s equation in a self-consistent way. Since the BAGEL scheme is based upon an exact reproduction of the moments of only the global strength distribution, it is not at all obvious that individual BAGEL poles of the Green’s function will be close.
to eigenenergies of the $(A \pm 1)$-electron system. In the discussion of the results, we will see that the BAGEL poles are spread out over a wide energy range, providing a satisfactory reproduction of the spectral distribution. Moreover, once convergence has been reached, one still has the possibility to lift the restriction of the number of poles and also redo the calculation one iteration further within the energy-bin method. This procedure allows for a smoother and more realistic distribution of the s.p. strength, as will be illustrated in the discussion of the results (section 3.6).

Now that we know what is the basic idea of the BAGEL scheme, let us have a closer look at how it can be used in the Dyson(2) scheme.

### 3.4.2 Transformation of Dyson’s equation into an eigenvalue problem.

The Dyson(2) scheme was developed to solve the second-order Dyson equation for the Green’s function and the corresponding self-energy. Both quantities are completely determined by means of their poles and residues and obey the Dyson equation (2.41).

It appears appropriate to solve this equation in matrix form [53]. Using the spectral (or Lehmann) representation of the Green’s function [see Eq. (2.18)], the Dyson equation can be transformed into the following two equations

\[
\sum_c [\delta_{ac} \varepsilon^H_{a} + \Sigma_c (\epsilon^{f}_{ak})] \langle 0(A) \mid c_c \mid k(A+1) \rangle = \epsilon^{f}_{ak} \langle 0(A) \mid c_a \mid k(A+1) \rangle
\]

\[
\sum_c [\delta_{ac} \varepsilon^H_{a} + \Sigma_c (\epsilon^{b}_{ak})] \langle k(A-1) \mid c_a \mid 0(A) \rangle = \epsilon^{b}_{ak} \langle k(A-1) \mid c_a \mid 0(A) \rangle. \quad (3.35)
\]

Assuming a diagonal self-energy, these relations simplify to

\[
\begin{align*}
\varepsilon^H_{a} + \Sigma_{a}(\epsilon_{ak}^{f}) &= \epsilon^{f}_{ak} \\
\varepsilon^H_{a} + \Sigma_{a}(\epsilon_{ak}^{b}) &= \epsilon^{b}_{ak}.
\end{align*}
\]  

(3.36)

We emphasize that the above relations represent non-linear equations, the graphical solution of which is shown schematically in Fig. 3.4. The self-energy appearing in Eq. (3.36) is determined unambiguously by its spectral representation Eq. (3.31) if the poles $(\omega^{f}_{j}, \omega^{b}_{j})$ and the corresponding residues $(\sigma^{f}_{j}, \sigma^{b}_{j})$ are known. When the form of Eq. (3.31) is substituted for the self-energy in Eq. (3.36) we arrive at

\[
\begin{align*}
\varepsilon^H_{a} + \sum_{j=1}^{D^f} \sigma^{f}_{j} (\epsilon_{ak}^{f} - \omega^{f}_{j}) + \sum_{j=1}^{D^b} \sigma^{b}_{j} (\epsilon_{ak}^{b} - \omega^{b}_{j}) &= \epsilon^{f}_{ak}, \\
\varepsilon^H_{a} + \sum_{j=1}^{D^f} \sigma^{f}_{j} (\epsilon_{ak}^{f} - \omega^{f}_{j}) + \sum_{j=1}^{D^b} \sigma^{b}_{j} (\epsilon_{ak}^{b} - \omega^{b}_{j}) &= \epsilon^{b}_{ak}. \quad (3.37)
\end{align*}
\]

In the present discussion, the infinitesimal parameter $\eta$ appearing in Eq. (3.31) will be discarded. Of course, Eq. (3.37) represents the generalized eigenvalue equation for
the self-energy of Eq. (3.28). It can now be shown easily (see also [58]) that solving the nonlinear equation (3.37) is equivalent to the diagonalization of the matrix $\mathcal{H}$ of dimension $D^b + D^f + 1$

$$
\begin{bmatrix}
\omega_{D^b}^b & 0 & \ldots & 0 & a_{D^b}^b & 0 & \ldots & 0 \\
0 & \omega_{D^b-1}^b & \ldots & 0 & a_{D^b-1}^b & 0 & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & \ldots & \omega_1^b & a_1^b & 0 & \ldots & 0 \\
a_{D^b}^f & a_{D^b-1}^f & \ldots & a_{1}^f & a_1^f & a_2^f & \ldots & a_{D^f}^f \\
0 & \ldots & 0 & 0 & a_2^f & 0 & \omega_2^f & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
0 & \ldots & 0 & a_{D^f}^f & 0 & 0 & \ldots & \omega_{D^f}^f \\
\end{bmatrix}
= 
\begin{bmatrix}
B_{D^b}^k \\
B_{D^b-1}^k \\
\vdots \\
B_1^k \\
a_1^f & a_2^f & \ldots & a_{D^f}^f \\
0 & 0 & \omega_2^f & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
0 & \ldots & 0 & \omega_{D^f}^f \\
\end{bmatrix}
$$

(3.38)

with $a_i^f = \sqrt{\sigma_i^f}$ and $a_i^b = \sqrt{\sigma_i^b}$. It is important to keep in mind that, in general, $D^b + D^f + 1$ is very large, as explained in the introduction to this section. It will be explained later how we can reduce the dimension of this matrix properly. In a more concise form, the eigenvalue equation (3.38) reads

$$
\mathcal{H}X_k = \varepsilon^{(2)}_{ak} X_k.
$$

(3.39)

By means of backward substitution, it is clear that Eq. (3.37) is the secular equation of Eq. (3.38). Note that $\varepsilon^{(2)}_{ak}$ can represent a forward energy $\varepsilon^F_{ak}$ or a backward energy $\varepsilon^B_{ak}$, depending on its position relative to the Fermi energy. As to the normalization of the eigenfunctions in Eq. (3.38), we impose that

$$
\sum_{j=1}^{D^f} |F_j^k|^2 + |X_0^k|^2 + \sum_{j=1}^{D^b} |B_j^k|^2 = 1,
$$

(3.40)

which implies that

$$
|X_0^k|^2 = \frac{1}{1 + \sum_{j=1}^{D^f} \frac{\sigma_j^f}{\varepsilon_{aj}^f - \omega_j^f} + \sum_{j=1}^{D^b} \frac{\sigma_j^b}{\varepsilon_{aj}^b - \omega_j^b}}.
$$

(3.41)

In the denominator of the right-hand side of this equation, we recognize the derivative of the self-energy. From the resemblance with Eq. (3.29), we see that we can determine the residue which corresponds to the eigenvalue $\varepsilon^{(2)}_{ak}$ by means of the $X_0^k$ component of the eigenvector. As a consequence, the solution of Eq. (3.38) yielding $D^b + D^f + 1$ eigenvalues and residues can be used to construct the spectral representation (3.20) of the Green's function. Note also that only the $X_0^k$ component
is required to determine the Green’s function; the quantities $B^k_i, i = 1, \ldots, D^b$ and $F^k_i, i = 1, \ldots, D^f$ are in fact superfluous entities, introduced to arrive at a genuine matrix eigenvalue equation, where the eigenvalue only appears on the right-hand side.

We illustrate this diagonalization procedure for the first iteration in the self-consistent process of the Dyson(2) scheme. In the first run, the second-order Green’s function is still a manageable expression as the summation in Eq. (3.23) is restricted to pure $2h1p$ and $2p1h$ excitations. This means that the poles and residues of the self-energy are simply $2h1p$ and $2p1h$ quantities and it is therefore possible to give the explicit form of the matrix elements in Eq. (3.38). The backward part is determined by

$$
\begin{align*}
\omega_i &= \epsilon_{h_1}^{HF} + \epsilon_{h_2}^{HF} - \epsilon_p^{HF} \\
a_i^b &= \left[ \sum_{LS} \frac{(2L+1)(2S+1)}{4(2\alpha + 1)} \right] \left| \langle apLS | W | h_1 h_2 LS \rangle \right|^2 \frac{1}{2},
\end{align*}
$$

where $h_1$ and $h_2$ are hole states (i.e. lying below the Fermi energy), $p$ is a particle state (lying above the Fermi surface), and $i$ is a short-hand notation for the configuration $(h_1 h_2 p)$.

Likewise, the forward part contains the following elements in the first iteration:

$$
\begin{align*}
\omega_i &= \epsilon_{p_1}^{HF} + \epsilon_{p_2}^{HF} - \epsilon_h^{HF} \\
a_i^f &= \left[ \sum_{LS} \frac{(2L+1)(2S+1)}{4(2\alpha + 1)} \right] \left| \langle ahLS | W | p_1 p_2 LS \rangle \right|^2 \frac{1}{2},
\end{align*}
$$

with $p_1$ and $p_2$ particle states, and $h$ a hole state [here $i$ stands for $(p_1 p_2 h)$]. After diagonalization, the HF s.p. state $a$ will be mixed up with the more complex $2h1p$ and $2p1h$ intermediary states (cf. the statement made at the end of the previous chapter). This causes the s.p. strength to be distributed over various discrete states. In the first iteration, only pure $2h1p$ and $2p1h$ excitations are taken into account. However, the increase of poles over the iterations mentioned before indicates that further iterations also include $3h2p$ ($3p2h$), $4h3p$ ($4p3h$), \ldots configurations.

To conclude this subsection, we elaborate somewhat more upon the residue or spectroscopic strength of the Green’s function. As indicated before [see Eq. (3.41)], this residue can be found from the $X_0$ component of the eigenvector which is a solution to Eq. (3.38). Here, we show how this identification can be found in another way. We recall the definition of the spectroscopic strength [see Eqs. (2.18) and (3.20)] for a diagonal Green’s function:

$$
S_0 [k (A + 1)] = | \langle 0(A) | c_a | k (A + 1) \rangle |^2 \\
S_0 [k (A - 1)] = | \langle k (A - 1) | c_a | 0(A) \rangle |^2,
$$

for a particle and a hole state respectively. To avoid complexity, we will restrict the discussion temporarily to the HF space combined with $2h1p$ excitations for a hole.
state and to the HF space combined with $2p1h$ excitations for a particle state. In this case, $|0(A)|$ in Eq. (3.44) represents the HF ground state and $| k(A+1) \rangle [k(A-1)]$ is an eigenstate obtained by diagonalizing the energy-matrix in Eq. (3.38) in $(A+1) [(A-1)]$ space, which is spanned by the particle state $c_a |0(A)\rangle$ [the hole state $c_a |0(A)\rangle$] and the $2p1h$ states $c_{p1}^\dagger c_{p2}^\dagger c_h |0(A)\rangle$ [the $2h1p$ states $c_p^\dagger c_h, c_h |0(A)\rangle$]:

$$| k(A+1) \rangle = X^k_0 c_a^\dagger |0(A)\rangle + \sum_{j(2p1h)} X^k_j (2p1h) c_{p1}^\dagger c_{p2}^\dagger c_h |0(A)\rangle$$

$$| k(A-1) \rangle = X^k_0 c_a |0(A)\rangle + \sum_{j(2h1p)} X^k_j (2h1p) c_p^\dagger c_h, c_h |0(A)\rangle. \quad (3.45)$$

From Eqs. (3.44) and (3.45), it is obvious that the square of $X^k_0$ is the residue of the corresponding pole of the Green's function. This statement still holds if we consider the problem (3.38) in HF space combined with $2h1p$ and $2p1h$ excitations. However, it requires techniques related to the random phase approximation (RPA) to prove this [59] and we do not consider these arguments here.

In the next subsection, we will discuss the Lanczos algorithm which is used in the BAGEL scheme to keep the number of poles over the iterations manageable.

### 3.4.3 Principles of the Lanczos scheme.

In the previous subsection, we have only restated the problem of solving Dyson's equation up to second order into a matrix eigenvalue equation: no approximations other than those mentioned in section 3.3 have been introduced. As discussed, in order to avoid the dimensionality problem, it is desirable to represent the Green's function using a lower number of poles $(M+N+1$ instead of $D^k + D^j + 1$) with conservation of the first few order moments. The Lanczos method is a very well-suited technique to find these poles and residues and is a fine algorithm especially when evaluating states of lowest energy, such as we are interested in in this work (ground-state energies, ionization energies, electron affinities, ...). If one tries to describe states which are relatively high in energy, the Lanczos scheme may not be as favorable a choice.

Let us now discuss the Lanczos algorithm ([57, 60, 61]), which transforms a general real and symmetric matrix $A$ into a tridiagonal form. Since the matrix $A$ is a representation of the operator $\hat{A}$ in some basis $\{|\varphi_i\rangle ; i = 0, \ldots, D\}$ ($A_{ij} = \langle \varphi_i | \hat{A} | \varphi_j \rangle$), the Lanczos algorithm can be regarded as a unitary transformation from the initial basis to another complete basis $\{|\phi_i\rangle ; i = 0, \ldots, D\}$, in which the matrix representation of $\hat{A}$ is tridiagonal.

The general procedure is as follows. First, we choose a starting vector $| \phi_0 \rangle$ as the first component of the new (to be constructed) basis set. This initial vector mostly
coincides with one of the initial basis states. In practice, that vector is chosen which shows the most simple physical structure, e.g., in the Dyson(2) scheme, we will always take the HF eigenvector obtained in the Dyson(1) scheme.

Once the starting vector \( |\phi_0\rangle \) is selected, we apply the operator \( \hat{A} \) to it and decompose the result in a component parallel and one orthogonal to \( |\phi_0\rangle \):

\[
\hat{A} |\phi_0\rangle = \alpha_1 |\phi_0\rangle + \beta_1 |\phi_1\rangle,
\]

with the condition \( \langle \phi_0 | \phi_1 \rangle = 0 \). This implies that the coefficients in the expansion are determined by

\[
\begin{align*}
\alpha_1 &= \langle \phi_0 | \hat{A} | \phi_0 \rangle, \\
\beta_1 &= \langle \phi_1 | \hat{A} | \phi_0 \rangle.
\end{align*}
\]

(3.47)

In these expressions, we assume that the basis vectors are normalized.

The next step consists of a decomposition of \( \hat{A} |\phi_1\rangle \):

\[
\hat{A} |\phi_1\rangle = \gamma_1 |\phi_0\rangle + \alpha_2 |\phi_1\rangle + \beta_2 |\phi_2\rangle,
\]

where \( \langle \phi_0 | \phi_2 \rangle = 0 \) and \( \langle \phi_1 | \phi_2 \rangle = 0 \). Since \( \hat{A} \) is a hermitian operator (\( \mathcal{A} \) is a real and symmetric matrix), we immediately see that \( \gamma_1 = \beta_1 \). The other coefficients are found via

\[
\begin{align*}
\alpha_2 &= \langle \phi_1 | \hat{A} | \phi_1 \rangle, \\
\beta_2 &= \langle \phi_2 | \hat{A} | \phi_1 \rangle.
\end{align*}
\]

(3.49)

In the next step, it becomes clear that the Lanczos algorithm leads to a tridiagonal structure:

\[
\hat{A} |\phi_2\rangle = \delta_1 |\phi_0\rangle + \gamma_2 |\phi_1\rangle + \alpha_3 |\phi_2\rangle + \beta_3 |\phi_3\rangle,
\]

(3.50)

where again the new vector \( |\phi_3\rangle \) is orthogonal to the previous ones. The orthogonality condition and the fact that \( \hat{A} \) is hermitian cause \( \delta_1 \) to vanish:

\[
\delta_1 = \langle \phi_0 | \hat{A} | \phi_2 \rangle = \alpha_1 \langle \phi_0 | \phi_2 \rangle + \beta_1 \langle \phi_1 | \phi_2 \rangle = 0.
\]

(3.51)

The other coefficients are given by expressions analogous to Eqs. (3.47) and (3.49).

Summarizing, if we take \( |\phi_0\rangle \) as a starting vector and put \( \alpha_1 = \langle \phi_0 | \hat{A} | \phi_0 \rangle \), \( \beta_0 = 0 \), then the coefficients in the expansion and the vectors of the basis set are generated by

\[
\begin{align*}
\beta_i &= ||(\hat{A} - \alpha_i) | \phi_{i-1} \rangle - \beta_{i-1} | \phi_{i-2} \rangle ||, \\
| \phi_i \rangle &= \frac{1}{\beta_i} [(\hat{A} - \alpha_i) | \phi_{i-1} \rangle - \beta_{i-1} | \phi_{i-2} \rangle], \\
\alpha_{i+1} &= \langle \phi_i | \hat{A} | \phi_i \rangle,
\end{align*}
\]

\[
\left\{ \begin{array}{l}
\end{array} \right.
\]
for \( i = 1, 2, \ldots, D \).

As a result of the Lanczos transformation, the matrix \( \mathcal{A} \) is cast in the form

\[
\mathcal{A} \rightarrow \begin{bmatrix}
\alpha_1 & \beta_1 & 0 & \ldots & \ldots & \ldots & 0 \\
\beta_1 & \alpha_2 & \beta_2 & 0 & \ldots & \ldots & 0 \\
0 & \beta_2 & \alpha_3 & \beta_3 & 0 & \ldots & 0 \\
\vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
\vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \ddots \\
0 & \ldots & 0 & \beta_{D-1} & \alpha_D & \beta_D \\
0 & \ldots & 0 & 0 & \beta_D & \alpha_{D+1}
\end{bmatrix}.
\]  

(3.52)

It is noted that the Lanczos algorithm equivalently amounts to a Gram-Schmidt orthogonalization of the basis \( \{ | \phi_0 \rangle, \hat{A} | \phi_0 \rangle, \ldots, \hat{A}^D | \phi_0 \rangle \} \) [62]. Diagonalization of (3.52) is therefore equivalent to a diagonalization of the matrix \( \mathcal{A} \) in the basis \( \{ | \phi_0 \rangle, \hat{A} | \phi_0 \rangle, \ldots, \hat{A}^D | \phi_0 \rangle \} \) (see also next subsection).

### 3.4.4 The BAGEL scheme.

After this explanation of the Lanczos algorithm, we now introduce the BAGEL (Basis GEnErated by Lanczos) scheme, that is founded on the Lanczos procedure. As specified in the introduction to this section, the goal of the BAGEL approach is to reduce a given distribution of poles and residues to a similar distribution of smaller dimension, such that the relevant physical properties remain conserved. In this subsection, we will explain how the BAGEL scheme works, i.e. how we can find the replacing (smaller) distribution. Also, we elaborate upon the reproduction properties intrinsic to the BAGEL scheme.

#### General principles and reproduction properties of the BAGEL scheme.

The Lanczos algorithm as discussed above is generally performed until the dimension of the new basis equals that of the old one. As indicated before, this implies that the transformation is unitary. However, we can also choose to stop the algorithm such that the dimension of the new orthogonal set is less than the original one. This variant of the Lanczos algorithm is sometimes called the BAGEL approach.

In general terms, the BAGEL scheme is used to replace the distribution of poles and residues \( (\sigma_j, \omega_j; J = 1, \ldots, D) \) by means of a smaller distribution \( (\tilde{\sigma}_j, \tilde{\omega}_j; j = 1, \ldots, I) \), where \( I \leq D \). To find the appropriate strengths and poles \( (\tilde{\sigma}_j, \tilde{\omega}_j) \) we construct a matrix \( \mathcal{A} \) (corresponding to operator \( \hat{A} \)) from the strengths and poles
(\(\sigma_J, \omega_J\)): 

\[
A = \begin{bmatrix}
\nu & a_1 & a_2 & \ldots & a_D \\
0 & a_1 & 0 & \ldots & 0 \\
0 & 0 & a_2 & \ldots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
0 & \ldots & \ldots & \ldots & a_D
\end{bmatrix},
\]

(3.53)

where we use the notation \(a_i = \sqrt{\sigma_i}\). The value of the parameter \(\nu\) is of no importance: it can be put to zero for the purposes of this part of the subsection, but we already introduced it here for future use.

The standard secular equation associated with the diagonalization of the operator \(\hat{A}\) reads:

\[
\hat{A} | X_k \rangle = \lambda_k | X_k \rangle, \quad k = 0, \ldots, D.
\]

(3.54)

Using the set of eigenvectors \(\{|X_k\rangle\}\), we can define the moment of order \(p\) of the operator \(\hat{A}\) with respect to a general vector \(|\psi\rangle\) as

\[
m(p) = \langle \psi | \hat{A}^p | \psi \rangle = \sum_{k=0}^{D} \langle \psi | \hat{A}^p | X_k \rangle \langle X_k | \psi \rangle = \sum_{k=0}^{D} \lambda_k^p | \langle \psi | X_k \rangle |^2.
\]

(3.55)

As discussed in the previous subsection, the Lanczos algorithm performs a basis transformation from the basis \(\{|\phi_i\rangle; i = 0, \ldots, D\}\) to another basis \(\{|\phi_i\rangle; i = 0, \ldots, D\}\). We now want to consider the generalized eigenvalue problem of the operator \(\hat{A}\) in the nonorthogonal basis \(\{|\phi_0\rangle, \hat{A} | \phi_0 \rangle, \ldots, \hat{A}^D | \phi_0 \rangle\}\), where \(|\phi_0\rangle\) is the vector we choose to start the BAGEL scheme (i.e., the first vector in the new basis set) because it will provide us with a means to find the replacing BAGEL poles. The generalized eigenvalue equation for the operator \(\hat{A}\) reads:

\[
\sum_{j=0}^{D} \langle i | \hat{A} | j \rangle X_{jk} = \lambda_k \sum_{j=0}^{D} S_{ij} X_{jk}, \quad i, k = 0, \ldots, D,
\]

(3.56)

where \(|i\rangle = \hat{A}^i | \phi_0 \rangle\). We normalize the vectors \(|X_k\rangle\) as follows: \(\langle X_i | S | X_j \rangle = \delta_{ij}\). In Eq. (3.56), \(S\) is a metric (overlap) matrix that enters the equation because of the nonorthogonality of the basis set:

\[
S_{ij} = \langle i | j \rangle = \langle \phi_0 | \hat{A}^i \hat{A}^j | \phi_0 \rangle
\]
\[
\begin{align*}
&= \sum_{k=0}^{D} \langle \phi_0 \mid \hat{A}^i \mid \lambda_k \rangle \langle \lambda_k \mid \hat{A}^j \mid \phi_0 \rangle \\
&= \sum_{k=0}^{D} \lambda_k^{i+j} \langle \phi_0 \mid \lambda_k \rangle \langle \lambda_k \mid \phi_0 \rangle \\
&= m(i + j), \ i, j = 0, \ldots, D, \tag{3.57}
\end{align*}
\]

making use of the complete set of eigenvectors \( | \lambda_k \rangle \) of the operator \( \hat{A} \) and the definition (3.55) of the moment \( m \) with respect to the vector \( | \phi_0 \rangle \). The matrix elements \( \langle i \mid \hat{A} \mid j \rangle \) can be written in terms of moments as well:

\[
\langle i \mid \hat{A} \mid j \rangle = \langle \phi_0 \mid \hat{A}^i \hat{A}^j \mid \phi_0 \rangle = m(i + j + 1), \ i, j = 0, \ldots, D. \tag{3.58}
\]

The representation of \( S_{ij} \) and \( \langle i \mid \hat{A} \mid j \rangle \) in terms of energy moments with respect to the starting vector \( | \phi_0 \rangle \) implies that if all moments up to order \( 2D + 1 \) of the exact distribution are known, we can construct the eigenvalue equation Eq. (3.56). After determining the \( D + 1 \) eigenvalues and eigenvectors, the moments of the operator \( \hat{A} \) can be recalculated and it will be found that they equal the original ones.

As noted before, the diagonalization process of \( \mathcal{A} \) in the adopted nonorthogonal basis is equivalent to applying the Lanczos procedure to \( \mathcal{A} \) and diagonalizing the resulting tridiagonal matrix. However, the BAGEL scheme consists of a truncation of the Lanczos algorithm after \( I \) iterations \( (I \leq D) \), i.e. when \( I + 1 \) vectors of the new basis are determined. It is clear that if we truncate the Lanczos algorithm after \( I \) iterations, the scheme will be equivalent to applying a Gram-Schmidt orthogonalization to \( \{ | \phi_0 \rangle, \hat{A} | \phi_0 \rangle, \ldots, \hat{A}^I | \phi_0 \rangle \} \). We will now demonstrate that with \( I + 1 \) vectors in the new basis set, we can reproduce the moments up to order \( 2I + 1 \) of the original matrix \( \mathcal{A} \) [Eq. (3.53)].

The generalized eigenvalue problem (3.56) in the truncated nonorthogonal basis \( \{ | \phi_0 \rangle, \hat{A} | \phi_0 \rangle, \ldots, \hat{A}^I | \phi_0 \rangle \} \) becomes

\[
\sum_{j=0}^{I} \langle i \mid \hat{A} \mid j \rangle \bar{X}_{jk} = \lambda_k \sum_{j=0}^{I} S_{ij} \bar{X}_{jk}, \ i, k = 0, \ldots, I. \tag{3.59}
\]

From the spectral decomposition of \( \hat{A} \) in terms of the truncated nonorthogonal basis, we obtain

\[
m(i + j + 1) = \langle i \mid \hat{A} \mid j \rangle = \sum_{k=0}^{I} \lambda_k \left[ S \bar{X}_k \right]_i \left[ S \bar{X}_k \right]^*_j, \ i, j = 0, \ldots, I. \tag{3.60}
\]

Next, we derive the following recurrence relation from Eq. (3.59):

\[
\sum_{j=0}^{I} m(i + 1 + j) \bar{X}_{jk} = (\lambda_k)^{i+1} \sum_{j=0}^{I} m(j) \bar{X}_{jk}, \ i, k = 0, \ldots, I; \tag{3.61}
\]
from which
\[
\left[ S \tilde{X}_k \right]_i = (\lambda_k)^i \left[ S \tilde{X}_k \right]_0, \quad i, k = 0, \ldots, I. \tag{3.62}
\]

This allows to cast Eq. (3.60) in the form
\[
m(i + j + 1) = \langle i \mid \hat{A} \mid j \rangle = \sum_{k=0}^{I} (\lambda_k)^{i+j+1} \left[ (S \tilde{X}_k) \right]_0^2 = \sum_{k=0}^{I} (\lambda_k)^{i+j+1} \left| \langle \phi_0 \mid S \mid \tilde{X}_k \rangle \right|^2, \quad i, j = 0, \ldots, I. \tag{3.63}
\]

From this we see that the approximative BAGEL residues and poles \((\tilde{\sigma}_j, \tilde{\omega}_j; j = 1, \ldots, I)\) can be found by solving Eq. (3.59): the eigenvalues \(\lambda_k\) represent the BAGEL poles, while \(\left| \langle \phi_0 \mid S \mid \tilde{X}_k \rangle \right|^2\) is the corresponding residue. The matrix constructed from these BAGEL poles and residues will generate the same moments \(0, \ldots, 2I + 1\) as the original matrix in Eq. (3.53), i.e. \(I\) iterations in the BAGEL scheme reproduce the first \(2I + 2\) order moments of the original matrix \(A\).

Now we also want to show that reproduction of the moments \(m\) of \(\mathcal{A}\) involves reproduction of the moments \(\mu\) of the distribution \((\sigma_j, \omega_j; J = 1, \ldots, D)\), from which \(A\) was derived. The latter moment is, evidently, defined as
\[
\mu(p) = \sum_{J=1}^{D} (\omega_j)^p \sigma_j = \sum_{J=1}^{D} (\omega_j)^p a_j^2. \tag{3.64}
\]

The connection between the moments \(m\) and \(\mu\) can be made in general terms by explicitly writing out the powers of the matrix \(A\) of Eq. (3.53) and taking the element in the first row and first column (here we adopt the usual convention that \(| \varphi_0 \rangle = | \phi_0 \rangle\)):
\[
m(0) = \langle \phi_0 \mid \hat{A}^0 \mid \phi_0 \rangle = (A^0)_{11} = 1
\]
\[
m(1) = \langle \phi_0 \mid \hat{A}^1 \mid \phi_0 \rangle = (A^1)_{11} = \nu
\]
\[
m(2) = \langle \phi_0 \mid \hat{A}^2 \mid \phi_0 \rangle = (A^2)_{11} = \nu^2 + \sum_{i=1}^{D} a_i^2 = \nu^2 + \mu(0)
\]
\[
m(3) = \langle \phi_0 \mid \hat{A}^3 \mid \phi_0 \rangle = (A^3)_{11} = \nu^3 + 2\nu \sum_{i=1}^{D} a_i^2 + \sum_{i=1}^{D} \omega_i a_i^2 = \nu^3 + 2\nu \mu(0) + \mu(1)
\]
\[
m(4) = \langle \phi_0 \mid \hat{A}^4 \mid \phi_0 \rangle = (A^4)_{11} = \nu^4 + 3\nu^2 \sum_{i=1}^{D} a_i^2 + \sum_{i=1}^{D} a_i^4 + 2\nu \sum_{j=1}^{D} \omega_j a_j^2 + \sum_{i=1}^{D} \omega_i^2 a_i^2
\]
\[
\nu^4 + 3\nu^2\mu(0) + \mu^2(0) + 2\nu\mu(1) + \mu(2).
\]

(3.65)

From this we see that conservation of the moments \( m \) of \( \mathcal{A} \) also leads to conservation of the moments \( \mu \) of \( (\sigma_j, \omega_j; J = 1, \ldots, D) \). However, there is an additional loss of two moments and \( J \) BAGEL iterations will conserve only the moments \( 0, \ldots, 2I - 1 \) of the original distribution \( (\sigma_j, \omega_j; J = 1, \ldots, D) \).

**Practical implementation of the BAGEL scheme.**

In this work, we use the BAGEL algorithm to reduce the dimension of the matrix \( \mathcal{H} \) in Eq. (3.38). As explained in subsection 3.4.2, the matrix \( \mathcal{H} \) consists of a backward and a forward part, which are related to the backward and forward part of the self-energy. The starting vector \( | \phi_0 \rangle \) for the BAGEL scheme will be the HF eigenvector of the state \( a \) we are considering. As indicated in the introduction to this section, we want to replace the backward \((\sigma^b_j, \omega^b_j; J = 1, \ldots, D^b)\) and forward \((\sigma^f_j, \omega^f_j; J = 1, \ldots, D^f)\) part of the distribution of the self-energy \( \Sigma^{(2)}_a(E) \) separately by a reduced distribution \((\tilde{\sigma}^b_j, \tilde{\omega}^b_j; j = 1, \ldots, N)\) and \((\tilde{\sigma}^f_j, \tilde{\omega}^f_j; j = 1, \ldots, M)\), defining the self-energy \( \tilde{\Sigma}^{(2)}_a(E) \). It was also explained that \( D^b + D^f + 1 \) becomes a very large number even after one or two iterations. Since we will put \( M \) and \( N \) to a value of about 20, it is clear that the reduction introduced by the BAGEL scheme is quite substantial. The practical implementation of the BAGEL scheme is now as follows.

It was demonstrated in the first part of this subsection that we can use the BAGEL technique to determine the replacing poles and residues. In fact, to speed up the algorithm, the construction of the truncated tridiagonal matrix corresponding to the matrix \( \mathcal{H} \) in Eq. (3.38) is implemented in two stages. As illustrated in Eq. (3.23), the self-energy actually consists of three summations over particle and hole states \( (b, c, d) \) and three summations (over \( j, k, l \)) corresponding to the spectral strength distribution of these states. At the first stage, we use the BAGEL technique to reduce the triple summation \( \Sigma_{j,k,l} \) to a single summation \( \Sigma_{\omega} \). To ensure that backward and forward part are treated on an equal footing, we apply the procedure for the backward and forward part of the self-energy separately, respectively with \( N \) and \( M \) BAGEL iterations. To find the replacing poles and residues, we only have to construct a matrix \( \mathcal{A}_b (\mathcal{A}_f) \) using the distribution \((\sigma^b_j, \omega^b_j) [(\sigma^f_j, \omega^f_j)]\) as in Eq. (3.53) (taking \( \nu = 0 \)). The index \( J \) in the distribution corresponds to the indices \((j, k, l)\) of Eq. (3.23) with fixed particle and hole states \((b, c, d)\). Then we apply the Lanczos procedure, truncate after \( N (M) \) iterations, and subsequently diagonalize the resulting tridiagonal matrix. The BAGEL poles are the eigenvalues found in the diagonalization and the corresponding residues can be obtained from the first component of the eigenvector [see Eq. (3.63)]. The \( N (M) \) iterations in
the BAGEL scheme will conserve the moments up to order $2N + 1$ ($2M + 1$) of $A_b$ ($A_f$). Returning to the self-energy distribution from which the matrices $A_b$ and $A_f$ were constructed, we have that $N$ ($M$) iterations conserve the moments of order $0, \ldots, 2N - 1$ ($2M - 1$) of the backward (forward) part of the self-energy separately [see Eqs. (3.33)-(3.34)].

After this first stage, the self-energy $\Sigma^{(2)}_a (E)$ is replaced by the self-energy $\tilde{\Sigma}^{(2)}_a (E)$ and the matrix $\mathcal{H}$ in Eq. (3.38) would be replaced by a matrix $\tilde{\mathcal{H}}$ of a smaller dimension (say $D^f + D^b + 1$). However, due to the triple summation $\sum_{b, c, d}$ over the particle and hole states this dimension is still too large and therefore, we have to reduce the dimension of backward and forward part once more. More specifically, we introduce the matrix $\tilde{\mathcal{H}}_b$ [cf. the upper left corner of $\mathcal{H}$ in Eq. (3.38)]

$$
\tilde{\mathcal{H}}_b = \begin{bmatrix}
\tilde{\omega}^b_{D^b_0} & 0 & \cdots & 0 & \tilde{a}^{b}_{D^b_0} \\
0 & \tilde{\omega}^b_{D^b_{-1}} & \cdots & 0 & \tilde{a}^{b}_{D^b_{-1}} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & \cdots & \tilde{\omega}^b_1 & \tilde{a}^{b}_1 \\
\tilde{a}^{b}_{D^b_0} & \tilde{a}^{b}_{D^b_{-1}} & \cdots & \tilde{a}^{b}_1 & \epsilon_{a}^{HF}
\end{bmatrix},
$$

(3.66)

and the matrix $\tilde{\mathcal{H}}_f$ [see the lower right corner of $\mathcal{H}$ in Eq. (3.38)]

$$
\tilde{\mathcal{H}}_f = \begin{bmatrix}
\epsilon_{a}^{HF} & \tilde{a}^f_1 & \tilde{a}^f_2 & \cdots & \tilde{a}^f_{D^f} \\
\tilde{a}^f_1 & \tilde{\omega}^f_1 & 0 & \cdots & 0 \\
\tilde{a}^f_2 & 0 & \tilde{\omega}^f_2 & \cdots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\tilde{a}^f_{D^f} & 0 & 0 & \cdots & \tilde{\omega}^f_{D^f}
\end{bmatrix}.
$$

(3.67)

The second stage in the reduction scheme now consists of applying the BAGEL algorithm to these matrices separately. Again, we truncate the BAGEL construction after $N$, respectively $M$ iterations. This leads to two sets of matrix elements ($\tilde{a}^b_i = \epsilon_{a}^{HF}, \tilde{a}^b_{i+1}, \tilde{\omega}^b_i; i = 1, \ldots, N$) and ($\tilde{a}^f_i = \epsilon_{a}^{HF}, \tilde{\alpha}^f_i, \tilde{\beta}^f_i; i = 1, \ldots, M$), constituting two tridiagonal matrices. Finally, we combine the tridiagonalized versions of the backward and forward part of $\tilde{\mathcal{H}}$ and obtain

$$
\tilde{\mathcal{H}} \rightarrow \begin{bmatrix}
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\
0 & \tilde{\beta}^b_2 & \tilde{\alpha}^b_3 & \tilde{\beta}^b_4 & \cdots & 0 \\
0 & \tilde{\beta}^b_3 & \tilde{\alpha}^b_4 & \tilde{\beta}^b_5 & \cdots & 0 \\
0 & \tilde{\beta}^b_4 & \tilde{\alpha}^b_5 & \tilde{\beta}^b_6 & \cdots & 0 \\
0 & \tilde{\beta}^b_5 & \tilde{\alpha}^b_6 & \tilde{\beta}^b_7 & \cdots & 0 \\
0 & \tilde{\beta}^b_6 & \tilde{\alpha}^b_7 & \tilde{\beta}^b_8 & \cdots & 0 \\
0 & \tilde{\beta}^b_7 & \tilde{\alpha}^b_8 & \tilde{\beta}^b_9 & \cdots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots
\end{bmatrix},
$$

(3.68)
This combined tridiagonal matrix is then diagonalized to find the $M + N + 1$ poles and residues of the Green’s function corresponding to $\tilde{\Sigma}_a^{(2)}(E)$. As to the conservation properties, we note that the second stage will reproduce the moments of order $0,\ldots,2N-1$ ($2M-1$) of the backward (forward) part of the self-energy $\tilde{\Sigma}_a^{(2)}(E)$ which was used to construct $\tilde{\mathcal{H}}$. As the first stage [yielded $\tilde{\Sigma}_a^{(2)}(E)$] already reproduced the moments of same order of the original self-energy $\Sigma_a^{(2)}(E)$, it is clear that the second stage does not affect the reproduction properties. The approach in which forward and backward part of the self-energy are replaced separately is referred to as the BAGEL($M,N$) scheme. In some systems it may be fortuitous to introduce a different number of poles for the forward and backward part, but in the present study, we will always have that $M = N$ in order to avoid complexity. Note that the BAGEL(0,0) approximation amounts to a HF-like approach.

**Reproduction of the moments of the total spectroscopic distribution.**

We will now find out what are the consequences for the Green’s function concerning the reproduction properties of the BAGEL scheme when we replace the self-energy $\Sigma_a^{(2)}(E)$ by its BAGEL($M,N$) approximation. Below, we will demonstrate that, although the BAGEL($M,N$) method reproduces the first $2N$, respectively $2M$ moments of the backward and forward part of the self-energy separately, only the first $2P + 2$ orders of the total spectroscopic strength of the Green’s function are reproduced, with $P = \min\{M,N\}$.

First, we will prove that in the diagonalization process of the tridiagonal matrix in (3.68), we do not reproduce the orders $0,\ldots,2(M + N) + 1$ of the total matrix $\tilde{\mathcal{H}}$, but only the moments $0,\ldots,2P + 1$, where $P = \min\{M,N\}$. Initially, we restrict the discussion to the common situation where $M = N$. If we choose the following identification for the initial vector $|\phi_0\rangle$ in the Lanczos algorithm

\[
|\phi_0\rangle \rightarrow \begin{bmatrix}
0 \\
\vdots \\
0 \\
1 \\
0 \\
\vdots \\
0
\end{bmatrix},
\]

(3.69)
we can consider the set of vectors given by:

\[
\left\{ \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}, \tilde{\mathcal{H}}^k_1, \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}, \tilde{\mathcal{H}}^k_2, \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix} : k = 1, \ldots, M \right\},
\]

which span the vector space \( \mathcal{V}(2M + 1) \). The matrices \( \tilde{\mathcal{H}}_1 \) and \( \tilde{\mathcal{H}}_2 \) are defined by the decomposition

\[
\tilde{\mathcal{H}} = \begin{bmatrix}
\tilde{\omega}^b_{D_0} & 0 & \cdots & 0 & \tilde{a}^b_{D_0} & 0 & \cdots & 0 \\
0 & \tilde{\omega}^b_{D_{n-1}} & \cdots & 0 & \tilde{a}^b_{D_{n-1}} & 0 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & \tilde{\omega}^f & \tilde{a}^f & 0 & \cdots & 0 \\
\tilde{a}^b_{D_0} & \tilde{a}^b_{D_{n-1}} & \cdots & \tilde{a}^b_{D_1} & \epsilon_{aa}^{HF} & \tilde{a}^f_1 & \tilde{a}^f_2 & \cdots & \tilde{a}^f_{D_I} \\
0 & 0 & \cdots & 0 & \tilde{a}^f_1 & \tilde{\omega}^f & 0 & \cdots & 0 \\
0 & 0 & \cdots & 0 & \tilde{a}^f_2 & 0 & \tilde{\omega}^f & 0 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & 0 & \tilde{a}^f_{D_I} & 0 & \cdots & 0 & \tilde{\omega}^f_{D_I} \\
\end{bmatrix}
\]

\[
= \tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2 - \epsilon_{aa}^{HF} \mathcal{U},
\]

where

\[
\tilde{\mathcal{H}}_1 = \begin{bmatrix}
\tilde{\omega}^b_{D_0} & 0 & \cdots & 0 & \tilde{a}^b_{D_0} & 0 & \cdots & 0 \\
0 & \tilde{\omega}^b_{D_{n-1}} & \cdots & 0 & \tilde{a}^b_{D_{n-1}} & 0 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & \tilde{\omega}^f & \tilde{a}^f & 0 & \cdots & 0 \\
\tilde{a}^b_{D_0} & \tilde{a}^b_{D_{n-1}} & \cdots & \tilde{a}^b_{D_1} & \epsilon_{aa}^{HF} & \tilde{a}^f_1 & \tilde{a}^f_2 & \cdots & \tilde{a}^f_{D_I} \\
0 & 0 & \cdots & 0 & \tilde{a}^f_1 & \tilde{\omega}^f & 0 & \cdots & 0 \\
0 & 0 & \cdots & 0 & \tilde{a}^f_2 & 0 & \tilde{\omega}^f & 0 & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & 0 & \tilde{a}^f_{D_I} & 0 & \cdots & 0 & \tilde{\omega}^f_{D_I} \\
\end{bmatrix}
\]
\[ \tilde{\mathcal{H}}_2 = \begin{bmatrix} 0 & \cdots & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & 0 & \hat{\alpha}_1^F & \hat{\alpha}_2^F & \cdots & \hat{\alpha}_{Df}^F \\ 0 & \cdots & 0 & \hat{\omega}_1^f & 0 & \cdots & 0 \\ 0 & \cdots & 0 & \hat{\omega}_2^f & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & 0 & \hat{\alpha}_{Df}^F & 0 & \cdots & \hat{\omega}_{Df}^f \end{bmatrix} \]

and

\[ U = \begin{bmatrix} 0 & \cdots & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & 0 & 0 & 0 & \cdots & 0 \\ 0 & \cdots & 0 & 1 & 0 & \cdots & 0 \\ 0 & \cdots & 0 & 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \cdots & 0 & 0 & 0 & \cdots & 0 \end{bmatrix} \]

\text{(3.72)}

The structure of the matrices \( \tilde{\mathcal{H}}_1 \) and \( \tilde{\mathcal{H}}_2 \) [compare with the matrices \( \tilde{\mathcal{H}}_a \) and \( \tilde{\mathcal{H}}_f \) of Eqs. (3.66) and (3.67)] implies that the vectors of the basis set (3.70) are those used as basis vectors when diagonalizing the matrix in Eq. (3.68). We will now show that the \( M \) vectors

\[
\begin{align*}
\left\{ \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix} \right\} \\
\left\{ \begin{bmatrix} 1 \\ \vdots \\ 0 \end{bmatrix} \right\} \\
\left\{ \begin{bmatrix} \vdots \\ \vdots \\ \vdots \end{bmatrix} \right\} \\
\left\{ \begin{bmatrix} 0 \\ 0 \end{bmatrix} \right\}
\end{align*}
\]

\text{(3.73)}

also belong to the vector space \( \mathcal{V}(2M + 1) \). In this way, we can relate information about the reproduction properties of the moments of \( \tilde{\mathcal{H}}_1 \) and \( \tilde{\mathcal{H}}_2 \) enclosed in the basis

\[
\left\{ | \phi_0 \rangle, \tilde{\mathcal{H}}_1 | \phi_0 \rangle, \tilde{\mathcal{H}}_2 | \phi_0 \rangle \ldots, \tilde{\mathcal{H}}_1^M | \phi_0 \rangle, \tilde{\mathcal{H}}_2^M | \phi_0 \rangle \right\}
\]

\text{(3.74)}

to information about the reproduction of the moments of \( \tilde{\mathcal{H}} \) enclosed in

\[
\left\{ | \phi_0 \rangle, \tilde{\mathcal{H}} | \phi_0 \rangle, \ldots, \tilde{\mathcal{H}}^M | \phi_0 \rangle \right\}.
\]

\text{(3.75)}
If the latter basis indeed spans a subspace of $\mathcal{V}(2M + 1)$, we know that in the diagonalization process of the matrix in Eq. (3.68) at least the moments $0, \ldots, 2M + 1$ of the total matrix $\tilde{\mathcal{H}}$ will be conserved. This property, namely that the basis (3.75) leads to a conservation of the first $2M + 2$ moments of $\tilde{\mathcal{H}}$, can be derived easily by applying the reasoning which followed Eq. (3.53) to $\tilde{\mathcal{H}}$ (in this case we put $\nu = \epsilon^H_a$ and $D = I = M$).

The proof uses the method of induction. To shorten the notation, we will represent the vector $[0 \ldots 0 \ 0 \ldots 0]^T$ by means of $[0 \ 0]^T$ in the following.

If $M = 1$, we have that

$$
\tilde{\mathcal{H}} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \tilde{\mathcal{H}}_1 \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} + \tilde{\mathcal{H}}_2 \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} - \epsilon^H_a \mathcal{U} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \tilde{\mathcal{H}}_1 \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} + \tilde{\mathcal{H}}_2 \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} - \epsilon^H_a \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \in \mathcal{V}(3). \quad (3.76)
$$

Now suppose that the premise is correct for $M = K - 1$, i.e.

$$
\tilde{\mathcal{H}}^k \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \in \mathcal{V}(2K - 1); \quad k = 1, \ldots, K - 1, \quad (3.77)
$$

then we have to prove that it is also correct for $M = K$. Since $\mathcal{V}(2K - 1) \subset \mathcal{V}(2K + 1)$, we only have to demonstrate that

$$
\tilde{\mathcal{H}}^K \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \in \mathcal{V}(2K + 1). \quad (3.78)
$$

We know that

$$
\tilde{\mathcal{H}}^K \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \tilde{\mathcal{H}} \tilde{\mathcal{H}}^{K-1} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}
$$

$$
= (\tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2 - \epsilon^H_a \mathcal{U}) \left\{ \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} + \sum_{k=1}^{K-1} (x_k^{(1)} \tilde{\mathcal{H}}^k_1 + x_k^{(2)} \tilde{\mathcal{H}}^k_2) \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \right\}, \quad (3.79)
$$

where $[x_0, x_k^{(1)}, x_k^{(2)}; k = 1, \ldots, K - 1]$ are expansion coefficients for the basis of $\mathcal{V}(2K - 1)$. Now it can be argued that all terms in Eq. (3.79) belong to $\mathcal{V}(2K + 1)$.
First, it is clear that

\[ x_0(\tilde{\mathcal{H}}_1 + \tilde{\mathcal{H}}_2 - \epsilon_a^{HF}\mathcal{U}) \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \in \mathcal{V}(2K + 1). \] (3.80)

Second, we see that

\[ \tilde{\mathcal{H}}_1 \tilde{\mathcal{H}}_2^k \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \text{ and } \tilde{\mathcal{H}}_2 \tilde{\mathcal{H}}_1^k \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \in \mathcal{V}(2K + 1), \] (3.81)

since \( k < K \). Furthermore, we have that

\[ \tilde{\mathcal{H}}_1 \tilde{\mathcal{H}}_2^k \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \tilde{\mathcal{H}}_1 \begin{bmatrix} 0 \\ b \\ C \end{bmatrix} = \begin{bmatrix} bV \\ b^a \epsilon_a^{HF} \\ 0 \end{bmatrix} = \tilde{b} \tilde{\mathcal{H}}_1 \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \in \mathcal{V}(2K + 1), \] (3.82)

where \( b \) is a constant and \( C \) is a constant vector of the appropriate dimension (their value is of no importance for the proof). Also, we introduced \( V = [\tilde{a}_{D_p}^k \tilde{a}_{D_{p-1}}^k \ldots \tilde{a}_D^k]^T \).

It is easy to see that we obtain something similar for \( \tilde{\mathcal{H}}_2 \tilde{\mathcal{H}}_1^k \). For the terms involving the matrix \( \mathcal{U} \), we have that

\[ \mathcal{U} \tilde{\mathcal{H}}_2^k \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \mathcal{U} \begin{bmatrix} 0 \\ b \\ C \end{bmatrix} = \begin{bmatrix} 0 \\ b \\ 0 \end{bmatrix} = \tilde{b} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \in \mathcal{V}(2K + 1), \] (3.83)

and alike for \( \mathcal{U} \tilde{\mathcal{H}}_1^k \), which proves the premise.

We now know that diagonalization in the basis

\[ \{ | \phi_0 \rangle, \tilde{\mathcal{H}}_1 | \phi_0 \rangle, \tilde{\mathcal{H}}_2 | \phi_0 \rangle, \ldots, \tilde{\mathcal{H}}_1^M | \phi_0 \rangle, \tilde{\mathcal{H}}_2^M | \phi_0 \rangle \} \] (3.84)

at least conserves the moments \( 0, \ldots, 2M + 1 \) of the total matrix \( \tilde{\mathcal{H}} \). We can also see easily that the moment of order \( 2M + 2 \) will not be reproduced correctly since the reasoning above can be extended to demonstrate that

\[ \tilde{\mathcal{H}}^{M+1} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \notin \mathcal{V}(2M + 1). \] (3.85)

Finally, if \( M \neq N \), it is clear from the derivation that the lower number of iterations will be the limiting factor in the scheme and therefore only the moments of order \( 0, \ldots, 2P + 1 \) with \( P = \min\{M, N\} \) of \( \tilde{\mathcal{H}} \) will be reproduced, which concludes the proof. This indicates that after the diagonalization of the tridiagonal
matrix in Eq. (3.68), only the moments of order 0, \ldots, 2P - 1 [and not the moments 0, \ldots, 2(M + N) - 1] of the total self-energy $\Sigma^{(2)}_a(E)$, which was used to construct $\hat{H}$, are reproduced.

As the solution of the eigenvalue equation corresponding to $\hat{H}$ yields the poles and residues of the Green’s function, it is clear from the proof above that the BAGEL(M,N) scheme will also conserve the moments of order 0, \ldots, 2P + 1 with $P = \min\{M,N\}$ of the total spectroscopic distribution of the Green’s function. We can see this more elegantly as well, by using Dyson’s equation explicitly and relating the reproduction of the moments of the self-energy distribution to the reproduction of the total spectroscopic distribution.

Let us put forward the following short-hand notations for the Green’s function and self-energy [compare with Eqs. (3.20) and (3.31) respectively]

$$G^{(2)}(E) = \sum_j \frac{S_j}{E - \epsilon_j}$$

$$\tilde{\Sigma}^{(2)}(E) = \sum_j \frac{\tilde{\sigma}_j}{E - \tilde{\omega}_j},$$

where the sums range over all poles, both backward and forward. Using this notation, the following relations between the distribution of the spectroscopic strength $(S_j, \epsilon_j)$ and the distribution of the self-energy strength $(\tilde{\sigma}_j, \tilde{\omega}_j)$ can be derived from Dyson’s equation (3.25):

$$E \to \infty \quad \Rightarrow \quad \sum_j S_j = 1,$$  \hspace{1cm} (3.87)

$$E \to \epsilon_j \quad \Rightarrow \quad \epsilon_j - e^{HF} = \sum_j \frac{\tilde{\sigma}_j}{\epsilon_j - \tilde{\omega}_j},$$  \hspace{1cm} (3.88)

$$E \to \tilde{\omega}_j \quad \Rightarrow \quad \sum_j \frac{S_j}{\tilde{\omega}_j - \epsilon_j} = 0.$$  \hspace{1cm} (3.89)

From the last two equations, we obtain:

$$\sum_j S_j(\epsilon_j - e^{HF}) = \sum_j \sum_j \frac{S_j \tilde{\sigma}_j}{\epsilon_j - \tilde{\omega}_j} = 0.$$  \hspace{1cm} (3.90)

Finally, we introduce the moments of order $k$ of the total distributions $(S_j, \epsilon_j)$ and $(\tilde{\sigma}_j, \tilde{\omega}_j)$:

$$M(k) = \sum_j S_j \epsilon_j^k,$$

$$\mu(k) = \sum_j \tilde{\sigma}_j \tilde{\omega}_j^k.$$  \hspace{1cm} (3.91)
We immediately see that \( M(0) = 1 \) [from Eq. (3.87)] and \( M(1) = e^{HF} \) [from Eq. (3.90)]. For the higher-order total moments \( (k \geq 2) \) we find

\[
M(k) = \sum_j S_j e^{k-1} \sum_j \frac{\tilde{\sigma}_j}{\epsilon_j - \tilde{\omega}_j} = \sum_j \tilde{\sigma}_j \sum_j S_j \left[ \frac{e^{k-1} - \tilde{\omega}_j^{k-1}}{\epsilon_j - \tilde{\omega}_j} + \frac{\tilde{\omega}_j^{k-1}}{\epsilon_j - \tilde{\omega}_j} \right] = \sum_{l=0}^{k-2} M(l) \mu_k \mu_l,
\]

where we have used Eqs. (3.88) and (3.89). From this relation between the total moments of the Green's function and the self-energy, we see that conservation of the moments \( 0, \ldots, 2P - 1 \) of the total self-energy involves conservation of the moments \( 0, \ldots, 2P+1 \) of the total spectroscopic distribution of the Green's function.

This concludes the discussion of the principles and reproduction properties of the BAGEL scheme. In the last part of this section, we will point out how additional correlations can be implemented in the Dyson(2) scheme.

### 3.4.5 Extension of the Dyson(2) scheme.

Typical examples of diagrams that are not taken into account in this work are in-medium screening effects, which modify the bare Coulomb interaction between the electrons. There are several ways to add these (and other) correlations to the Dyson(2) scheme. A first method is to include a certain amount of correlation already in the orbitals that set up the (quasi-)complete basis set. An example of this idea is the *Brueckner-Bethe-Goldstone approach*, where the states appearing in the \( 2h1p \) (\( 2p1h \)), \ldots configurations of the Dyson(2) scheme would no longer be noninteracting HF states, but result from a more complicated calculation in which e.g. the bare Coulomb interaction is replaced by an effective interaction as obtained from the Bethe-Goldstone equation (see e.g. Ref. [63] for an application of this technique). Note, however, that an approach in which the \( 2h1p \) (\( 2p1h \)) configurations are not described in terms of HF states must be implemented with great care in order to avoid double counting of the diagrams (see e.g. [54]).

Also, we should mention the random phase approximation (RPA, see e.g. Ref. [2]) as a handsome method to add interactions to the scheme. We do not discuss this extension here, as it is beyond the scope of the present work. Two examples of diagrams that are not included in the Dyson(2) scheme, but that can be incorporated via the methods mentioned above, are sketched in Fig. 3.5.

Another technique which tries to “dress” the interaction between the electrons (in order to account for screening) is the so-called *GW-approximation*. It is inspired on
the same ideas as the Brueckner-Bethe-Goldstone approach. For an explanation on the technique, we refer to [64]-[67]. The GW-method is common practice in the study of the electron gas and condensed matter (see e.g. [68]-[71]), but it can be applied to finite systems as well. As an example, we mention the work by E.L. Shirley and R.M. Martin [72] who studied atomic systems using the GW-method. More specifically, they focused on some group-III elements (boron, aluminium, and gallium), as well as alkali-like ions and transition-metal elements. Using these results they made a study of core-valence correlation effects, which were subsequently incorporated in a parametrized core-polarization potential that can be used in e.g. pseudopotential theory [73].

Finally, we note that a straightforward method to add interactions between the different configurations in our scheme is simply to make the matrix in Eq. (3.38) less sparse. We then replace Eq. (3.38) by

\[
\begin{bmatrix}
H_{2h1p} & a_b & 0 \\
\bar{a}_b & \epsilon_{a}^{HF} & \bar{a}_f \\
0 & a_f & H_{2p1h}
\end{bmatrix}
\begin{bmatrix}
B \\
X_k^b \\
F
\end{bmatrix}
= \epsilon_2^{(2)}
\begin{bmatrix}
B \\
X_k^b \\
F
\end{bmatrix}.
\]  

(3.93)

We can take into account interactions in $2h1p$-configuration space and $2p1h$-configuration space by making the matrices $H_{2h1p}$ and $H_{2p1h}$ non-diagonal. The two blocks in the matrix in Eq. (3.93) which are zero indicate that no interactions between the $2h1p$ and $2p1h$ blocks are considered. If required, these blocks can be replaced by nonzero elements as well. Note, however, that in this work, we only consider eigenvalue problems of the form of Eq. (3.38): Eq. (3.93) is reported merely as an example of a possible extension.

Finally, all tools to solve Dyson’s equation have been explained. Let us now have a look at the construction of the basis set used in actual calculations before discussing the results for closed-shell atomic systems.
3.5 Construction of the atomic basis set.

In this section, we reveal how the basis set to tackle Dyson’s equation was constructed. Ideally, we would work with an infinite number of basis-set functions, but numerical considerations impose a truncation. The dimension of the basis set is also very closely related to the wall parameters $C_l$ and $R_l$ introduced in Eq. (3.19). Generally speaking, if the wall is put closer to the atomic center, less basis functions are required to span a certain energy range, but the influence of the wall on the results will be more prominent. As explained in section 3.2, the last of the three steps in the first-order algorithm serves to diminish the role of the wall. The success of this step largely depends on the degree of completeness of the basis set. If the wall is close to the nucleus, more orbitals will be required for an accurate description of the Dyson(1) value.

On the other hand, if the wall is put too far from the nucleus, the sampling introduced by the wall is not performed in a fair way; too much weight is spent in the lower region of the continuum and again a large basis set would be required to cover an appropriate energy range into the continuum. We therefore have to find a trade-off between the dimension of the basis set and the error introduced by the discretization wall. We will demonstrate in this section that basis-set dimension and wall parameters are optimized such that the error is out of the range of required accuracy. The discussion of the optimum choice for wall parameters and number of orbitals will be held in a thorough way for the $s$- and $p$-orbitals only. For the other $l$ values we will solely provide evidence that for the selected parameters, the ionization energy is indeed converged in terms of the basis set and the wall parameters.

To determine the number of wave functions in the basis set, the following scheme is used. First of all, the strength $C_l$ of every wall is kept fixed at value of five atomic units. The distance parameter $R_l$ offers enough freedom for our purposes. The practical completeness of the basis set and the tuning of the wall distances were checked by the convergence of two results: the ionization energy as predicted in HF and the same observable after one iteration in the second-order scheme. We concentrated on the energy of the highest occupied HF $s$,p. orbital, because that appeared to be the most difficult level to reproduce. The reason to restrict the convergence check to the first iteration in the second-order scheme, is that in that case, the dimensionality problem mentioned in section 3.4 is not yet an issue. In first iteration, we are only dealing with pure $2h1p$ and $2p1h$ excitations and therefore the number of poles in the self-energy is still manageable: the first iteration can be performed without the BAGEL scheme. For each $l$-value, a typical basis-set optimization consists of fixing the wall parameters and then gradually increasing the number of wave functions. This procedure is then repeated with other wall parameters until a good choice has been found.

We will now give a detailed overview of the construction of the set in case of magne-
Table 3.1: Ionization energies (in a.u.) of Mg in Dyson(1) [between brackets] and in first iteration of Dyson(2) for varying numbers of $s$- and $p$-wave functions in the basis set and with the wall parameters fixed ($s$-wall at 6 a.u., $p$-wall at 3 a.u., and strength of the walls 5 a.u.).

<table>
<thead>
<tr>
<th></th>
<th>p+15</th>
<th>p+20</th>
<th>p+25</th>
<th>p+30</th>
<th>p+45</th>
</tr>
</thead>
<tbody>
<tr>
<td>s+15</td>
<td>0.25979</td>
<td>0.26036</td>
<td>0.26060</td>
<td>0.26072</td>
<td>0.26080</td>
</tr>
<tr>
<td></td>
<td>(0.24751)</td>
<td>(0.24751)</td>
<td>(0.24751)</td>
<td>(0.24751)</td>
<td>(0.24751)</td>
</tr>
<tr>
<td>s+20</td>
<td>0.26119</td>
<td>0.26177</td>
<td>0.26203</td>
<td>0.26215</td>
<td>0.26225</td>
</tr>
<tr>
<td></td>
<td>(0.24944)</td>
<td>(0.24944)</td>
<td>(0.24944)</td>
<td>(0.24944)</td>
<td>(0.24944)</td>
</tr>
<tr>
<td>s+25</td>
<td>0.26199</td>
<td>0.26257</td>
<td>0.26284</td>
<td>0.26297</td>
<td>0.26307</td>
</tr>
<tr>
<td></td>
<td>(0.25063)</td>
<td>(0.25063)</td>
<td>(0.25063)</td>
<td>(0.25063)</td>
<td>(0.25063)</td>
</tr>
<tr>
<td>s+30</td>
<td>0.26245</td>
<td>0.26304</td>
<td>0.26331</td>
<td>0.26344</td>
<td>0.26356</td>
</tr>
<tr>
<td></td>
<td>(0.25138)</td>
<td>(0.25138)</td>
<td>(0.25138)</td>
<td>(0.25138)</td>
<td>(0.25138)</td>
</tr>
<tr>
<td>s+45</td>
<td>0.26300</td>
<td>0.26359</td>
<td>0.26387</td>
<td>0.26401</td>
<td>0.26413</td>
</tr>
<tr>
<td></td>
<td>(0.25241)</td>
<td>(0.25241)</td>
<td>(0.25241)</td>
<td>(0.25241)</td>
<td>(0.25241)</td>
</tr>
<tr>
<td>s+75</td>
<td>0.26320</td>
<td>0.26379</td>
<td>0.26407</td>
<td>0.26421</td>
<td>0.26434</td>
</tr>
<tr>
<td></td>
<td>(0.25292)</td>
<td>(0.25292)</td>
<td>(0.25292)</td>
<td>(0.25292)</td>
<td>(0.25292)</td>
</tr>
<tr>
<td>s+85</td>
<td>0.26322</td>
<td>0.26381</td>
<td>0.26409</td>
<td>0.26422</td>
<td>0.26436</td>
</tr>
<tr>
<td></td>
<td>(0.25300)</td>
<td>(0.25300)</td>
<td>(0.25300)</td>
<td>(0.25300)</td>
<td>(0.25300)</td>
</tr>
</tbody>
</table>

It is our intention to explain how the basis sets were constructed, to indicate that it is indeed complete for practical purposes, and to convince the reader of the numerical stability of the results. We require the ionization energy to be converged within $1 \times 10^{-4}$ or $2 \times 10^{-4}$ atomic units.

The magnesium atom consists of 12 electrons, which result in a HF ground-state configuration of $(1s^22s^22p^63s^2)$. For the convergence of the HF ionization energy, only the number of $s$- and $p$-wave functions is relevant. Therefore, we restrict to these types of orbitals first.

The HF value for the energy of the last occupied state as predicted by Fischer [47] is $-0.25305$ a.u. (experimentally $-0.2811$ a.u. is found [74]). The root mean square radius of the $3s$ and $2p$ wave functions is 3.253 a.u. and 0.684 a.u., respectively. This gives an idea on how close we can put the wall: it is advisory to turn on the wall at a much larger distance than 3 atomic units.

In Tables 3.1, 3.2, and 3.3 we find the Dyson(1) (between brackets) and the first iteration Dyson(2) value for wall distances ($R_0 = 6; R_1 = 3$), ($R_0 = 10; R_1 = 7$),
Table 3.2: Ionization energies (in a.u.) of Mg in Dyson(1) [between brackets] and in first iteration of Dyson(2) for varying numbers of s- and p-wave functions in the basis set and with the wall parameters fixed (s-wall at 10 a.u., p-wall at 7 a.u., and strength of the walls 5 a.u.).

<table>
<thead>
<tr>
<th></th>
<th>p+15</th>
<th>p+20</th>
<th>p+25</th>
<th>p+30</th>
<th>p+35</th>
</tr>
</thead>
<tbody>
<tr>
<td>s+15</td>
<td>(0.25284)</td>
<td>(0.25284)</td>
<td>(0.25284)</td>
<td>(0.25284)</td>
<td>(0.25284)</td>
</tr>
<tr>
<td>s+20</td>
<td>0.26421</td>
<td>0.26422</td>
<td>0.26423</td>
<td>0.26423</td>
<td>0.26424</td>
</tr>
<tr>
<td>s+25</td>
<td>0.26427</td>
<td>0.26429</td>
<td>0.26429</td>
<td>0.26430</td>
<td>0.26430</td>
</tr>
<tr>
<td>s+30</td>
<td>0.26429</td>
<td>0.26431</td>
<td>0.26432</td>
<td>0.26433</td>
<td>0.26433</td>
</tr>
<tr>
<td>s+35</td>
<td>0.26425</td>
<td>0.26431</td>
<td>0.26433</td>
<td>0.26434</td>
<td>0.26435</td>
</tr>
<tr>
<td>s+45</td>
<td>0.26431</td>
<td>0.26434</td>
<td>0.26435</td>
<td>0.26436</td>
<td>0.26436</td>
</tr>
</tbody>
</table>

and \( R_0 = 14; R_1 = 11 \) respectively (as stated above, the wall strength is kept at 5 a.u.). Concerning notation, s+15 for instance, means that we added 15 unoccupied s-states to the 3 occupied HF wave functions \( 1s, 2s, \) and \( 3s \).

There are a few general features to be observed in these tables. First, it appears that the difference between two adjacent columns is roughly independent of the row. Manifestly, the orbitals of different angular momentum add to the completeness of the basis set in a more or less independent way. This can be expected in a HF picture, but the excitations in the second-order scheme allow for mixing between states of different \( l \) (as long as the global angular momentum \( L \) remains conserved of course). Nevertheless, in first iteration this interference is apparently not strong enough to make the shift between rows dependent of the column and *vice versa*.

Second, we see that the Dyson(2) result is more sensitive to changing the number of orbitals than Dyson(1). This is not surprising: in the Dyson(2) scheme, the orbitals in the continuum play a more active role (particles are excited into continuum states and fall back again). Mathematically, the different role of the continuum in the Dyson(1) scheme and the Dyson(2) scheme is evident from Eqs. (2.46) and (2.47): the energy denominators appearing in the second-order self-energy include both bound as well as continuum states, while the first-order self-energy is energy-independent. Furthermore, in Dyson(1), the number of orbitals is only important to make the basis set complete if the set is far from completeness, the outcome for the
3.5. *Construction of the atomic basis set.*

Table 3.3: Ionization energies (in a.u.) of Mg in Dyson(1) [between brackets] and in first iteration of Dyson(2) for varying numbers of s- and p-wave functions in the basis set and with the wall parameters fixed (s-wall at 14 a.u., p-wall at 11 a.u., and strength of the walls 5 a.u.).

<table>
<thead>
<tr>
<th></th>
<th>p+15</th>
<th>p+20</th>
<th>p+30</th>
<th>p+35</th>
<th>p+66</th>
</tr>
</thead>
<tbody>
<tr>
<td>s+15</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
</tr>
<tr>
<td>s+20</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
</tr>
<tr>
<td>s+25</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
</tr>
<tr>
<td>s+30</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
</tr>
<tr>
<td>s+35</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
</tr>
<tr>
<td>s+45</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
</tr>
<tr>
<td>s+54</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
<td>(0.25306)</td>
</tr>
</tbody>
</table>

bound states in the third step of the Dyson(1) algorithm will differ significantly from that in the first step in the scheme. In this sense, orbitals in the continuum have a less active role than in Dyson(2). Finally, we note that the three choices of the wall distance eventually lead to the same converged value [Dyson(1): 0.25(30) - 0.25(31) a.u.; Dyson(2): 0.26(43)6 a.u.]. This shows that, in the end, the basis set reaches completeness in the three cases and that the description of the self-energy $\Sigma^{(2)}(E)$ converges to a limit value, independent of the choice of the confining potential.

However, the required number of orbitals (note that in Table 3.1 up to 85 additional s- and 45 p-orbitals are needed) and the speed of convergence varies largely between the tables. We chose the wall parameters of Table 3.2 as optimum values. Within the desired range of accuracy (±1.5 × 10^{-4} a.u.), we note that adding 20 orbitals to both the occupied s- and p-orbitals is certainly satisfying for Dyson(2). Also, it will turn out that the impact of adding wave functions with higher l is larger than adding more s- and p-states. A check on the HF value reveals that for this choice, it is converged to the coordinate space HF result.

Of course, if we add higher l orbitals to the s- and p-wave functions, the completeness of the basis set still improves. Note that all orbitals we add to the basis
set are from now on unoccupied. This means that they will only affect the Dyson(2) result and as a consequence, this variable will be the sole criterion in selecting the appropriate wave functions with angular momentum higher than unity.

In Table 3.4, the energies are collected that appear when adding \( d \)- and \( f \)-states. The \( d \)-wall is put at a distance of five a.u. and the \( f \)-wall at three atomic units. A good selection seems adding 20 \( d \)-states and 15 \( f \)-states.

What is the effect if we add \( g \)- and \( h \)-orbitals to this basis? The results are collected in Table 3.5, where the wall distances are one a.u. and zero a.u. respectively.

Table 3.4: Ionization energies of Mg (in a.u.) in first iteration of Dyson(2) when adding \( d \)- and \( f \)-wave functions to the basis set with 23 \( s \)-waves and 21 \( p \)-waves.

<table>
<thead>
<tr>
<th></th>
<th>( f+0 )</th>
<th>( f+5 )</th>
<th>( f+10 )</th>
<th>( f+15 )</th>
<th>( f+20 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d+10 )</td>
<td>0.27288</td>
<td>0.27347</td>
<td>0.27459</td>
<td>0.27468</td>
<td>0.27470</td>
</tr>
<tr>
<td>( d+15 )</td>
<td>0.27296</td>
<td>0.27446</td>
<td>0.27471</td>
<td>0.27480</td>
<td>0.27484</td>
</tr>
<tr>
<td>( d+20 )</td>
<td>0.27299</td>
<td>0.27449</td>
<td>0.27474</td>
<td>0.27484</td>
<td>0.27488</td>
</tr>
<tr>
<td>( d+25 )</td>
<td>0.27301</td>
<td>0.27450</td>
<td>0.27476</td>
<td>0.27486</td>
<td>0.27490</td>
</tr>
</tbody>
</table>

Table 3.5: Ionization energies of Mg (in a.u.) in first iteration of Dyson(2) when adding \( g \)- and \( h \)-wave functions to the basis set.

<table>
<thead>
<tr>
<th></th>
<th>( h+0 )</th>
<th>( h+5 )</th>
<th>( h+10 )</th>
<th>( h+15 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g+5 )</td>
<td>0.27522</td>
<td>0.27535</td>
<td>0.27543</td>
<td>0.27547</td>
</tr>
<tr>
<td>( g+10 )</td>
<td>0.27538</td>
<td>0.27552</td>
<td>0.27560</td>
<td>0.27565</td>
</tr>
<tr>
<td>( g+15 )</td>
<td>0.27545</td>
<td>0.27559</td>
<td>0.27568</td>
<td>0.27572</td>
</tr>
<tr>
<td>( g+20 )</td>
<td>0.27548</td>
<td>0.27562</td>
<td>0.27571</td>
<td>0.27575</td>
</tr>
</tbody>
</table>

We conclude that we can add 15 \( g \)- and 10 \( h \)-orbitals to \( \{(s+20)[10;5], (p+20)[7;5], (d+20)[5;5], (f+15)[3;5]\} \), resulting in a first iteration value for the Dyson(2) ionization energy of 0.27568 atomic units (in the notation for the basis set, we include the wall parameters \( R_i \) and \( C_i \) between square brackets).

Adding \( i \)- and \( j \)-orbitals, we arrive at the values of Table 3.6 (the walls are placed at zero distance from the nucleus). We see that adding five \( i \)-orbitals has the same effect as adding five more \( g \)- and five more \( h \)-orbitals to \( \{(s+20)[10;5], (p+20)[7;5], (d+20)[5;5], (f+15)[3;5], (g+15)[1;5], (h+10)[0;5]\} \). From Table 3.6,
Table 3.6: Ionization energies of Mg (in a.u.) in first iteration of Dyson(2) when adding i- and j-wave functions to the basis set.

<table>
<thead>
<tr>
<th></th>
<th>j+0</th>
<th>j+5</th>
<th>j+10</th>
</tr>
</thead>
<tbody>
<tr>
<td>i+5</td>
<td>0.27575</td>
<td>0.27579</td>
<td>0.27582</td>
</tr>
<tr>
<td>i+10</td>
<td>0.27579</td>
<td>0.27584</td>
<td>0.27586</td>
</tr>
<tr>
<td>i+15</td>
<td>0.27581</td>
<td>0.27586</td>
<td>0.27588</td>
</tr>
</tbody>
</table>

It is obvious that adding j- orbitals is not necessary. As a consequence, we can regard \{(s + 20)[10;5], (p + 20)[7;5], (d + 20)[5;5], (f + 15)[3;5], (g + 15)[1;5], (h + 10)[0;5], (i + 5)[0;5]\} as our final basis set, predicting a first-iteration result for the ionization energy of 0.27575 atomic units. This basis set has a dimension of 109 orbitals and is one of the largest of the closed-shell atoms. For the open-shell case, however, the basis sets will even be far larger, putting an additional payload on the calculations. How this increase was coped with for the open-shell atoms will be explained in chapter 4.

Table 3.7: Reproduction of the ionization energy of Mg in first iteration of Dyson(2) using a varying number of BAGEL poles.

<table>
<thead>
<tr>
<th>number of poles</th>
<th>result (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.26722</td>
</tr>
<tr>
<td>10</td>
<td>0.27238</td>
</tr>
<tr>
<td>15</td>
<td>0.27488</td>
</tr>
<tr>
<td>20</td>
<td>0.27551</td>
</tr>
<tr>
<td>25</td>
<td>0.27569</td>
</tr>
</tbody>
</table>

Finally, we still have to determine the number of poles to use in the BAGEL scheme. It was not needed to let the number of forward \(M\) and backward \(N\) poles differ, i.e. the BAGEL(M,M) scheme gives fair enough a description of the many-electron systems in this study. The number \(M\) of poles in the forward and backward region is determined again by performing the first-iteration calculation of the Dyson(2) scheme, but this time, of course, switching on the BAGEL approximation. We let the number of BAGEL poles vary until the result of the previous calculation without the BAGEL scheme (i.e. 0.27575 a.u.) is reproduced acceptably. Table 3.7 displays the evolution for five up to 25 BAGEL poles. We risk
numerical inaccuracies in the BAGEL(M,M) scheme if we let $M$ increase above 25. However, it is observed that 25 poles for both forward and backward part suffice for a reproduction of the actual result within the proposed accuracy. We also see that the result is converged in terms of the number of BAGEL poles. This was the case for all closed-shell atoms: $20 - 25$ BAGEL poles were enough to achieve a fair reproduction of the genuine first-iteration ionization energy. Note that already in first iteration of the Dyson(2) scheme (0.27560 a.u.), the ionization energy is closer to experiment (0.2811 a.u.) than HF (0.25291 a.u.), but this, of course, can be due to a fortuitous coincidence: only the converged Dyson(2) values are to be compared with experiment.

Table 3.8: Basis sets needed for a suitable discretization of the continuum.

<table>
<thead>
<tr>
<th>$l=0$</th>
<th>He</th>
<th>Be</th>
<th>Ne</th>
<th>Mg</th>
<th>Ar</th>
<th>Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_l$</td>
<td>$C_l$</td>
<td>3s</td>
<td>1s</td>
<td>2s</td>
<td>1s</td>
<td>3s</td>
</tr>
<tr>
<td>$\text{occ.}$</td>
<td></td>
<td>2s - 21s</td>
<td>2s - 21s</td>
<td>2s - 21s</td>
<td>2s - 21s</td>
<td>2s - 21s</td>
</tr>
<tr>
<td>$l=1$</td>
<td>$R_l$</td>
<td>$C_l$</td>
<td>3s</td>
<td>3s</td>
<td>4s</td>
<td>4s</td>
</tr>
<tr>
<td>$\text{occ.}$</td>
<td></td>
<td>3d - 12d</td>
<td>3d - 12d</td>
<td>3d - 12d</td>
<td>3d - 12d</td>
<td>3d - 12d</td>
</tr>
<tr>
<td>$l=2$</td>
<td>$R_l$</td>
<td>$C_l$</td>
<td>3s</td>
<td>3s</td>
<td>4s</td>
<td>4s</td>
</tr>
<tr>
<td>$\text{occ.}$</td>
<td></td>
<td>5s - 9s</td>
<td>5s - 9s</td>
<td>5s - 9s</td>
<td>5s - 9s</td>
<td>5s - 9s</td>
</tr>
<tr>
<td>$l=3$</td>
<td>$R_l$</td>
<td>$C_l$</td>
<td>3s</td>
<td>3s</td>
<td>4s</td>
<td>4s</td>
</tr>
<tr>
<td>$\text{occ.}$</td>
<td></td>
<td>6s - 10h</td>
<td>6s - 10h</td>
<td>6s - 10h</td>
<td>6s - 10h</td>
<td>6s - 10h</td>
</tr>
<tr>
<td>$l=4$</td>
<td>$R_l$</td>
<td>$C_l$</td>
<td>3s</td>
<td>3s</td>
<td>4s</td>
<td>4s</td>
</tr>
<tr>
<td>$\text{occ.}$</td>
<td></td>
<td>7s - 11i</td>
<td>7s - 11i</td>
<td>7s - 11i</td>
<td>7s - 11i</td>
<td>7s - 11i</td>
</tr>
<tr>
<td>$l=5$</td>
<td>$R_l$</td>
<td>$C_l$</td>
<td>3s</td>
<td>3s</td>
<td>4s</td>
<td>4s</td>
</tr>
<tr>
<td>$\text{occ.}$</td>
<td></td>
<td>8l - 12l</td>
<td>8l - 12l</td>
<td>8l - 12l</td>
<td>8l - 12l</td>
<td>8l - 12l</td>
</tr>
</tbody>
</table>

To finalize this discussion on the construction of the basis sets, we collect the sets selected for all closed-shell atoms of the study in Table 3.8, along with the value for the wall parameters.

### 3.6 Results.

In this section, we present results of the calculations on closed-shell systems. The selected set of atoms consists of a number of small systems where HF is a good starting point, e.g. He and Ne. On the other hand, we chose Be and Mg as examples of atomic systems where the HF approach is known to produce less accurate results, especially in a finite-basis-set approach. We also performed calculations on heavier
atomic systems such as Ar and Kr to see whether relativistic corrections are really needed to meet the experimental data ([75],[76]). In addition, we include standard HF, post-HF and Density Functional Theory (DFT) calculations performed with the GAUSSIAN 98 package [77] on the same set of atoms using a localized Gaussian basis set. As functionals for DFT, we will use the popular BLYP and B3LYP functionals, while the basis set is the HF/6-311g** set. The post-HF methods include electron correlations by means of different perturbation schemes such as Møller-Plesset perturbation theory (MP2, MP4) or configuration interaction (CI). In-depth information on these methods can be found in e.g. ref. [12]. A thorough discussion is given of the various trends observed in the results of this large variety of many-body techniques. We should note however that a detailed comparison between the various basis-set oriented methods is somewhat troublesome due to the sometimes large influence of the basis set on the results. We only mention the HF, post-HF and DFT calculations as a means to compare with our Dyson(1) and Dyson(2) scheme, to identify certain trends and to indicate that the efforts implemented in the self-consistent calculations can generate an important shift towards the experimental value.

3.6.1 Influence of the second-order correlations on the s.p. strength and total energy.

As discussed above, the second-order Dyson equation is solved self-consistently in an iterative scheme [referred to as Dyson(2)]. In the HF approach [referred to as Dyson(1)] the spectral function

$$ S_{\alpha}(E) = S_{\alpha}^p(E) + S_{\alpha}^h(E), $$

(3.94)

with [see Eqs. (2.20) and (2.21)]

$$ S_{\alpha}^p(E) = \sum_{j_{(A+1)}} | \langle 0(A) | c_{\alpha} | j(A+1) \rangle |^2 \delta \left( E - E_{j(A+1)} + E_{0(A)} \right) $$

(3.95)

and

$$ S_{\alpha}^h(E) = \sum_{j_{(A-1)}} | \langle 0(A) | c_{\alpha}^1 | j(A-1) \rangle |^2 \delta \left( E + E_{j(A-1)} - E_{0(A)} \right), $$

(3.96)

concentrates all strength in one peak located at the HF s.p. energy. In the Dyson(2) scheme, however, we notice already in first iteration a depletion of the strength in the HF peak (see Fig. 3.6 for the case of the neon atom). The remaining strength is distributed over $2p1h$ and $2h1p$ states as a result of the energy dependence of the second-order self-energy. The effect of self-consistency is to gather the many small satellites of the first iteration in a smaller amount of more important poles. The energy of the quasi-particle pole (the highest peak in Fig. 3.6) varies only little from
Figure 3.6: Spectral function of the 2p orbital in Ne in HF [Dyson(1)] and in Dyson(2).

first iteration to convergence, which is obtained after three to five iterations. The general trend set by the first iteration is maintained, and as a rule of thumb we can say that one pole carries about 90% of the strength.

In Table 3.9 we present the first ionization energies as predicted by various schemes. It is noted from the first two numerical columns that DFT does a poor job predicting the atomic ionization energy. A possible reason for this failure may be that in the fit of the functionals, less emphasis is put unto the asymptotic region, which is however crucial for an accurate description of the ionization energy. This will be elaborated upon in chapters 5 and 6. We should stress however, that the figures in the table are calculated from an optimization of the atom only: we did not optimize atom and positive ion separately and then subtract the total energies. In the latter case, the DFT predictions would be much better. The third and fourth column give the HF estimates obtained with GAUSSIAN 98 and Dyson(1) respectively. We note that the two schemes agree very well, which indicates that the energies in the GAUSSIAN numerical package are a good approximation to coordinate-space HF. However, some of the predictions may differ from the experimental values in a substantial way. It is striking that the corrections resulting from the first iteration of the Dyson(2) scheme are such that experimental agreement is almost reached. We
Table 3.9: First ionization energies for some atomic systems (a.u.). Dyson(1) stands for the configuration-space solution of the HF equations, (as discussed in section 3.2, these results are very close to the solution of HF in coordinate space). Dyson(2) gives the solution of Dyson’s equation in second order after one and two iterations and after convergence.

<table>
<thead>
<tr>
<th>Element</th>
<th>DFT-DZ</th>
<th>DFT-DZLYP</th>
<th>HF(6-311g**+)</th>
<th>Dyson(1)</th>
<th>Dyson(2)</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.576</td>
<td>0.578</td>
<td>0.574</td>
<td>0.517</td>
<td>0.518</td>
<td>0.506</td>
</tr>
<tr>
<td>Ne</td>
<td>0.360</td>
<td>0.304</td>
<td>0.305</td>
<td>0.260</td>
<td>0.260</td>
<td>0.250</td>
</tr>
<tr>
<td>Mg</td>
<td>0.148</td>
<td>0.194</td>
<td>0.153</td>
<td>0.176</td>
<td>0.177</td>
<td>0.174</td>
</tr>
<tr>
<td>Ar</td>
<td>0.270</td>
<td>0.457</td>
<td>0.290</td>
<td>0.279</td>
<td>0.284</td>
<td>0.283</td>
</tr>
<tr>
<td>Kr</td>
<td>0.333</td>
<td>0.383</td>
<td>0.324</td>
<td>0.326</td>
<td>0.355</td>
<td>0.360</td>
</tr>
</tbody>
</table>

notice that higher iterations until convergence only have a smoothing effect on the results (see also Fig. 3.6). It is observed that for Be (and to a smaller degree Mg), the ionization energy is best reproduced in first iteration and then worsens due to convergence. This may be caused by the diagonality approximation of the Green’s function, which, though its effect was negligible in first iteration, might play a role of importance in the highly correlated Be system. We also see from the table that for Be and Mg, the correlations embedded in the second-order scheme are overestimated in first iteration: the evolution towards convergence is oscillatory. For Kr, it is clear that screening and relativistic effects must have a major impact on the predictions: it is the only atom for which the Dyson(1) result is closer to experiment than Dyson(2).

Similar conclusions can be drawn for the total binding energies of the atomic systems. Contrary to what would be expected for a two-body operator, knowledge of the dressed s.p. Green’s functions for each orbital suffices to calculate the total binding energy with inclusion of all correlations implemented in Dyson(2) ([83], [84])

\[
E_{0(A)} = \frac{1}{2} \sum_{a} \int dE \text{ Tr} \{ (H_0 + E) G(E) \}, \tag{3.97}
\]

where \( \text{Tr} \) stands for the trace operation and \( H_0 \) denotes the one-body part (kinetic energy and external field) of the Hamiltonian of the system. This so-called Koltun sum rule or Galitskii-Migdal formula [85] can be employed provided that the basis set used is complete and solely one- and two-body interactions are present in the system. The contour in the integration of Eq. (3.97) should enclose all ionization poles of the Green’s function. More explicitly, the equation can be cast in the form (\( N \) is the number of backward BAGEL poles)

\[
E_{0(A)} = \frac{1}{2} \sum_{a=1}^{N_b} \sum_{j=1}^{N} \sqrt{\langle a | H_0 | a \rangle + \epsilon_{a,j} b} \ S^{(b)}_{a,j}, \tag{3.98}
\]
The advantage of this sum rule is that it yields the total ground state of the system when the backward part of the s.p. Green's function is known. Yet, it has the drawback of not being variational. Another way to calculate the total energy using Green’s functions is to use the Luttinger-Ward formula [86]. However, the Luttinger-Ward energy functional is not explicit, i.e. the approach involves knowledge of the self-energy as a functional in the Green’s function. Therefore the energy functional is not easy to calculate for common physical systems like atoms. The energy functional is derived from a diagrammatic expansion and expressed as a functional in the Green’s function. The Luttinger-Ward method is a variational approach however, in the sense that the energy functional is constructed such that the first derivative with respect to the Green’s function is zero when evaluated with the self-consistent Green’s function of a given truncation of the self-energy series (see also ref. [87]).

The numerical results for the total energy as predicted by Dyson(1) and Dyson(2) for the atomic systems under consideration are collected in Table 3.10. In addition, we also consider the HF ground-state energies as obtained by using a localized Gaussian basis set. From the table and from Fig. 3.7, we notice that the Dyson(1) prediction can be regarded as the limit of all HF results using finite basis sets. Perturbation schemes beyond HF involve additional correlations allowing for a

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Be</th>
<th>Ne</th>
<th>Mg</th>
<th>Ar</th>
<th>Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT-B3LYP</td>
<td>-2.913</td>
<td>-14.671</td>
<td>-128.951</td>
<td>-200.093</td>
<td>-527.553</td>
</tr>
<tr>
<td>HF</td>
<td>HF/6-311g**</td>
<td>-2.860</td>
<td>-14.572</td>
<td>-128.523</td>
<td>-199.607</td>
<td>-526.807</td>
</tr>
<tr>
<td></td>
<td>Dyson(1)</td>
<td>-2.862</td>
<td>-14.573</td>
<td>-128.549</td>
<td>-199.617</td>
<td>-526.826</td>
</tr>
<tr>
<td>Dyson(2)</td>
<td>first it.</td>
<td>-2.890</td>
<td>-14.633</td>
<td>-128.709</td>
<td>-199.751</td>
<td>-527.075</td>
</tr>
<tr>
<td></td>
<td>conv.</td>
<td>-2.890</td>
<td>-14.628</td>
<td>-128.888</td>
<td>-199.948</td>
<td>-527.422</td>
</tr>
</tbody>
</table>
Figure 3.7: Binding energies in helium as obtained in various schemes. The results are separated into three classes according to the use of basis sets (HF, post-HF, CI), to the solution in coordinate space or complete basis sets [Dyson(1), Dyson(2)] and to the use of the density-functional concept.
larger binding and achieving a better agreement with experiment. As could be expected, configuration interaction (CI) determines the limit for this class of post-HF perturbation schemes. Involving more correlations by definition, Dyson(2) is obviously superior to CI for all atomic systems under consideration, and approaches the experimental situation very well, even in first iteration. For neon, we note an exception: there the CI prediction is better than the first-iteration Dyson(2) result. However, the converged result again favors the Dyson(2) scheme. Again, beryllium shows a pattern differing from the other atoms: as for the first ionization energy, the first-iteration result is closer to experiment than the converged result. We tend to attribute this deficiency to the diagonal approximation as well.

Only the DFT results can rival the Green's function method in describing the total binding energy, but the former scheme is beyond the set of microscopic theories due to the implementation of functionals which have a (partially) empirical character. In fact, it is not surprising that the predictive power of DFT prevails on that of Dyson(2) in all cases considered here. The Becke correction [89] of the BLYP functional [90] has been determined by a least-squares fit to the atomic HF data of the six noble-gas atoms helium through radon. The B3LYP functional [91] should be regarded as an extension of the BLYP functional with exchange-correlation corrections, where the coefficients have been fit to a large number of ionization energies, proton affinities, and atomic energies. Due to the larger training set, we notice some slightly larger deviations from the experimental noble-gas data under study in this work.

In conclusion, it should be stressed that the experimental agreement is surprisingly well achieved in the Dyson(2) scheme, which succeeds in generating about 50% to 75% of the correlation energy. Only a small fraction of the total ground-state energy is missing and this is probably due to either additional higher-order correlations not involved in the second-order approach or the diagonality approximation of Green's function and self-energy.

3.6.2 Single-particle energies and strengths.

Single-particle energies and occupation probabilities as resulting from a number of computational methods and experimental estimates are presented in Table 3.11. The s.p. energies and spectroscopic strengths of the valence shells are accessible experimentally by means of electron momentum spectroscopy (EMS). This method consists of scattering an electron on an atomic target with a sufficiently high energy to knock out one of the electrons of the atom. From the spectrum of the two outgoing particles, information can be gained on the ionization energies and the spectroscopic strength. An excellent survey of this experimental technique can be found in references [98]-[100].

All experimental values given in Table 3.11 are taken from the references [92]-[97] and compared with the theoretical predictions of various models which are funda-
Table 3.11: Single-particle properties. The experimental energies and occupation numbers of the valence states can be found in [92, 93, 94] for Ne, Ar, and Kr respectively, while the energies for the core orbitals of Be and Ne are taken from ref. [95], for Mg and Ar from [96] and [97], and for Kr from [95] and [97]. The experimental energy for He is taken from ref. [78]. The Dyson(2) predictions are the results after convergence.

<table>
<thead>
<tr>
<th></th>
<th>s.p. energies</th>
<th>spectroscopic strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT-BLYP</td>
<td>DFT-B3LYP</td>
</tr>
<tr>
<td>He 1s</td>
<td>0.578</td>
<td>0.558</td>
</tr>
<tr>
<td>2s</td>
<td>-0.209</td>
<td>-0.271</td>
</tr>
<tr>
<td>Ne 1s</td>
<td>-35.48</td>
<td>-36.93</td>
</tr>
<tr>
<td>2s</td>
<td>-1.398</td>
<td>-1.435</td>
</tr>
<tr>
<td>3s</td>
<td>-0.460</td>
<td>-0.550</td>
</tr>
<tr>
<td>Mg 1s</td>
<td>-46.24</td>
<td>-46.79</td>
</tr>
<tr>
<td>3p</td>
<td>-1.076</td>
<td>-1.833</td>
</tr>
<tr>
<td>3s</td>
<td>-0.168</td>
<td>-0.194</td>
</tr>
<tr>
<td>Ar 1s</td>
<td>-114.3</td>
<td>-115.1</td>
</tr>
<tr>
<td>3s</td>
<td>-0.875</td>
<td>-0.968</td>
</tr>
<tr>
<td>3p</td>
<td>-0.570</td>
<td>-0.472</td>
</tr>
<tr>
<td>Kr 1s</td>
<td>-511.8</td>
<td>-512.7</td>
</tr>
<tr>
<td>2s</td>
<td>-66.41</td>
<td>-67.13</td>
</tr>
<tr>
<td>2p</td>
<td>-60.12</td>
<td>-60.71</td>
</tr>
<tr>
<td>4s</td>
<td>-5.658</td>
<td>-5.235</td>
</tr>
</tbody>
</table>

mentally different from each other. We present HF results on two different levels: the HF/6-311g** level, i.e., the HF scheme solved with a triple-zeta polarized basis set [12] and Dyson(1) which reproduces the exact HF values as solved in coordinate space. In experiment, the energy levels are distinguished by using the total angular momentum quantum number $j$. To allow for comparison, we made an average over the experimental levels with the same principal and angular momentum quantum number. Apparently, the use of a localized basis set does not cause significant discrepancies with the exact HF values. On the contrary, the mutual agreement is even surprisingly good. Taking into account correlations involved in the second-order self-energy, it seems to bring the s.p. energies closer to the experimental values. Some s.p. orbitals become more deeply bound, others evolve to a less bound pattern. The spectroscopic strengths of the highest occupied orbitals vary from 0.90 to 0.96, in agreement with
experiment. The deviation of the spectroscopic strength from the HF value is a conspicuous measure for the amount of correlation present in the system. For normal electron systems, deviations are generally rather small. For nucleon systems and liquid systems (e.g., liquid helium) on the other hand, correlations are more important and a larger depletion of the hole states may occur [101]. Note that the calculations confirm the general statement mentioned at the end of the previous chapter. We indeed find levels with a spectroscopic strength close to unity around the Fermi level: the quasi-particles. It is interesting to see that due to the interaction with the nucleus, the orbital closest to the atomic center (1s) assumes a more s.p.-like character as well. Between the 1s levels and the levels at the Fermi energy, we find states with a (relatively) large fragmentation.

Although the correlations do become more and more important as the atomic number increases, it may be concluded that the depletion \(1 - \sum_{j=1}^{M} S_j^{(0)}\) of the orbitals remains moderate on the average. This may indicate that the short-range correlations of the Coulomb force between two electrons in the atomic medium (in the presence of other electrons) are relatively weak. We notice two significant discrepancies between theory and experiment in Table 3.11: the 3s level in Ar and the 4s level in Kr, where the experiment predicts a large fragmentation of the spectroscopic strength to 0.55-0.51. The failure of our theory to reproduce this particular feature is probably due to the fact that the second-order self-energy is evaluated consistent with the first-order self-energy, i.e. with propagators reflecting the HF problem in the neutral atom and, in particular, no adjustment of the s.p. HF energies (e.g. a scaling to the experimental values before use in a second-order calculation) is performed. Some authors (see e.g. [102]) are able to reproduce the experimental fragmentation pattern by using the so-called frozen core s.p. energies and wave functions for the unoccupied electron orbitals. This involves that the occupied orbitals which form the HF core are calculated using a self-consistent HF procedure. The continuum levels, on the other hand, are calculated in the field of a singly or doubly ionized positive ion. It is not clear how this can be incorporated in the framework of a self-consistent Green's function theory. However, taking into account screening diagrams in the second-order self-energy may alleviate the error in the spectroscopic strength for these orbitals. Some elegant approaches to take into account screening diagrams have been mentioned in section 3.4.5.

For more deeply bound orbitals, we do find some substantial spreading of the spectroscopic strength (except for 1s states). The 2s-orbital in Mg shows two poles with almost equal strength. We applied the energy-bin method (see section 3.4) to this orbital after convergence was reached in the BAGEL approach. The resulting hole-spectral function is displayed in Fig. 3.8. In contrast to the BAGEL approach where the strength is mainly concentrated into a few poles (two poles in case of the 2s orbital in Mg, see Table 3.11), the spectral function obtained in the energy bin
method presents a more realistic picture of the s.p. strength distribution.

![Graph of 2s in Mg (energy bin method)](image)

Figure 3.8: Spectral function of the 2s orbital in Mg in Dyson(2) using the energy-bin method after convergence in the BAGEL scheme.

The case of Kr reveals the breakdown of the nonrelativistic approximation. Starting from the HF value, the 4s energy predicted in Dyson(2) approaches the experimental value in the right direction, whereas the 4p energy deviates from it.

### 3.6.3 One-particle density and self-energy.

To conclude this chapter, we will also discuss some other properties of the many-body system that are extremely important in this work, namely the total density and the second-order self-energy.

First, let us concentrate on the influence of the correlations on the one-particle density of the system, defined as [see also Eq. (2.26); \( \eta \) again denotes an infinitesimal positive convergence parameter]

\[
\rho (r) = \frac{1}{2\pi i} \int dE \ e^{iE \eta} G(r, r, E) = \frac{1}{2\pi i} \int dE \ e^{iE \eta} \sum_a \phi_a^* (r) G_a (E) \phi_a (r)
\]
\[
\phi_{\alpha}(r) \phi_{\beta}(r) \sum_j S_{\alpha_0}^{(b)}(r) = \sum_a \phi_{\alpha}^{(a)}(r) \phi_{\beta}^{(a)}(r) \sum_j S_{\alpha_0}^{(b)}(r),
\]
which is normalized as
\[
4\pi \int dr \, r^2 \rho(r) = A.
\]
Note that the one-body density of the \( A \)-particle system is completely determined by the spectroscopic strength of the \((A - 1)\) system.

We display the HF, the Dyson(1) and the correlated Dyson(2) density of argon in Fig. 3.9, which elegantly reveals the typical shell structure of the atom [in fact, \( r^2 \rho(r) \) is shown in the figure]. With the HF density, we mean the density which follows from the first step in the Dyson(1) algorithm, i.e. where the HF problem is solved in coordinate space for the bound states only. The Dyson(1) density is the density which results from the third step, in which the HF equations are solved in the truncated basis set. In the region for \( r = 0 \rightarrow 3 \) a.u., it is noted that the difference

![Figure 3.9: Dyson(1) and Dyson(2) densities of Ar in coordinate space. Inset: difference between Dyson(2) and Dyson(1) density in atomic units.](image)

between Dyson(1) and Dyson(2) is very small (see inset Fig. 3.9). It is well-known
that in an electron system the correlation effect is much smaller than the influence of exchange. Yet, it is of extreme importance to achieve accurate predictions (in the sense of reaching chemical accuracy, i.e. an error of about 0.0434 eV = 0.0016 a.u. = 1 kcal/mole) for the properties of chemical systems. We also notice that the differences are larger between shells than in a shell: the largest deviation occurs between shells with $n = 2$ and $n = 3$.

Let us now focus on the range $r = 3 \rightarrow 4.5$ atomic units. It is then observed that the tail of Dyson(1) and Dyson(2) ground-state densities is different. This is due to the different ionization energy as predicted by the two schemes. It is intuitively obvious that the asymptotic behavior of the ground-state density is dominated by the least bound HF orbital (see also e.g. [103]). The asymptotic behavior of this orbital is determined by its s.p. energy, i.e. the ionization energy:

$$
\rho(r) \rightarrow |\phi_{0(A-1)}(r)|^2 \\
\rightarrow r^{2(\frac{1}{2}-1)}e^{-2\kappa r},
$$

(3.101)

where $\kappa = \sqrt{-2\epsilon_{\text{ion}}}$ and $-\epsilon_{\text{ion}} = I = E_{0(A-1)} - E_{0(A)}$ is the ionization energy. This will be elaborated upon in chapter 6.

Finally we note that the Dyson(2) density eventually suffers from finite-basis set effects: the density no longer decays (as good as) exponentially when a critical radius is reached, but saturates to a plateau. Mind, however, that also the Dyson(1) and even the HF density saturate to a plateau, but at a (much) larger distance than Dyson(2). In the Dyson(1) and Dyson(2) schemes, the plateau is induced by the confining wall in the Dyson(1) scheme, while for the HF density, it only arises due to boundary effects and is situated near to $r_{\text{max}} = 50$ atomic units. The plateaus extend over a certain range, after which the density decays faster than exponentially. It is clear that due to the harmonic oscillator confining wall introduced in the Dyson(1) scheme, the density will eventually behave in a gaussian-like way. The distances at which the plateau starts for the Dyson(1) and Dyson(2) scheme are determined by the accuracy to which the bound HF levels are determined. Changing the dimension of the basis set causes the critical radius to move. This indicates that numerical errors, a.o. due to the truncation of the basis and the discretization of the continuum, have a noticeable effect on the asymptotic region of the density. Another argument for the fact that the basis set generates some deficiencies can be found by comparing the HF and the Dyson(1) density. In the former case, the density decays exponentially over the whole range shown in the figure, while for the latter the decay becomes faster than exponential from a radius of about five atomic units.

There is also a more fundamental reason for the plateau. In general, we can expand the nondiagonal one-body density as

$$
\rho(\vec{r}, \vec{r}'') = \sum_\alpha n_\alpha \phi_\alpha(\vec{r}) \phi^*_\alpha(\vec{r}''),
$$

(3.102)
where \( n_\alpha \) is the occupation number of state \( \alpha \) and \( \phi_\alpha(r) \) is the HF approximation to the natural orbitals as obtained in our Dyson(1) scheme. Focussing on the continuum states in the sum, we see that if the eigenenergy of the state increases, \( \phi_\alpha(r) \) will assume a more plane-wave like character and the contribution to the nondiagonal density will only depend in the difference of the space coordinates:
\[
\sum_{\alpha=\alpha_{\min}}^{\infty} n_\alpha e^{i\mathbf{k}_\alpha \cdot (\mathbf{r}'-\mathbf{r})},
\]
such that a constant contribution to the diagonal one-body density arises: \( \sum_{\alpha=\alpha_{\min}}^{\infty} n_\alpha \). The appearance of the plateau in the Dyson(2) density is therefore also induced by our approximation of the natural orbitals by the HF orbitals in a truncated basis set: in the complete set of the genuine natural orbitals, there would be no constant contribution to the diagonal one-body density.

Since for the selected basis sets, the critical radius in the Dyson(2) density is large (4.5 a.u. in case of argon and about the same value for the other atoms) and the density is already very small at that distance, this phenomenon does not deteriorate the predictive power of the Dyson(2) scheme. However, when we use these densities to construct the exchange-correlation potential of Density Functional Theory (the inversion problem, see chapter 6), it will be necessary to correct for this pathology.

The last discussion of this chapter is devoted to the second-order self-energy. As indicated, this quantity is a complex and energy-dependent function that is nonlocal in coordinate space (but, within the diagonal approximation of section 3.3, assumed local in the configuration space of HF orbitals). We will now study the self-energy for argon as a function of the energy for two states near the Fermi energy: the highest occupied (3p) and lowest unoccupied (4s) orbitals. As mentioned in the previous chapter and as follows from Table 3.11, these states are special because they have a relatively large life time and thus the imaginary part is relatively small.

According to the well-known identity of Eq. (2.22), the self-energy of Eq. (3.23) can be analyzed in a real part and an imaginary part:

\[
Re\{\Sigma_a^{(2)}(E)\} = \sum_{b,c,d} \frac{F_{abc,d}}{4(2l_a+1)} \sum_{j,k,l} \left\{ \frac{S_{c,j}S_{b,j}S_{d,k}S_{b,k}}{E - (e_{c,j} + e_{d,k} - e_{b,l})} + \frac{S_{c,j}^*S_{b,j}S_{d,k}^*S_{b,k}^*}{E - (e_{c,j}^* + e_{d,k}^* - e_{b,l}^*)} \right\},
\]

\[
Im\{\Sigma_a^{(2)}(E)\} = \pi \sum_{b,c,d} \frac{F_{abc,d}}{4(2l_a+1)} \sum_{j,k,l} \left\{ S_{c,j}^*e_{b,j}S_{d,k}^*S_{b,k}^* \delta(E - (e_{c,j}^* + e_{d,k}^* - e_{b,l}^*)) - S_{c,j}e_{b,j}S_{d,k}S_{b,k} \delta(E - (e_{c,j} + e_{d,k} - e_{b,l})) \right\}.
\]

(3.103)

The real part represents a dispersive second-order correction to the (real and energy-independent) HF potential. As noted before, the imaginary part is a measure for the spreading and the life time of state \( a \). Therefore, it is also responsible for the
3.6. Results.

Depletion of the hole states, typical for correlated systems.

From Eq. (3.103), we note that real and imaginary part of the self-energy obey a Kramers-Kronig ([104]-[105]) relation. Indeed, using Eq. (2.22), the following equation is derived

\[ Re\{\Sigma_a(E)\} = \frac{1}{\pi} \mathcal{P}_v \int_{-\infty}^{\infty} dE' \frac{Im\{\Sigma_a^{(b)}(E')\}}{E - E'} - \frac{1}{\pi} \mathcal{P}_v \int_{e_f}^{\infty} dE' \frac{Im\{\Sigma_a^{(f)}(E')\}}{E - E'}, \]  

(3.104)

where we have the same notations for backward and forward part of the self-energy as in Eqs. (3.35) and (3.36), and where \( \mathcal{P}_v \) stands for the principal value of the integral (see also chapter 2).

Based on this observation, a convenient way to derive the energy representation of the self-energy is obtained. In general, the real part is calculated using Eq. (3.104) from the knowledge of the imaginary part. We illustrate this process for the two orbitals in argon nearest to the Fermi level. In Figs. 3.10 and 3.11, we show the imaginary part of the self-energy and the corresponding real part as calculated using the Kramers-Kronig relation (3.104). In the figures, backward, forward and total contributions are shown separately.

Note that, for a finite system, the imaginary part consists of a discrete sum of \( \delta \)-distributions. We can, however, for reasons of presentation (and to simulate limited resolution of experimental equipment) replace the \( \delta \)-distribution by a Lorentz distribution with width \( \Delta \) \[ \delta(E) \to \frac{\Delta}{\pi} \frac{\Delta}{(E - \Delta/2)^2 + \Delta^2} \]  

(3.105)

This method is used to show the self-energy components in Figs. 3.10 and 3.11. Note that for the forward imaginary part, the sign has been included in the graph.

We should also mention that for an infinite fermion system, it can be shown that, to all orders in perturbation theory, \( Im\{\Sigma_a^{(2)}(e)\} = C_a(e - \epsilon_F)^2 \) (see e.g. [107]). This was shown for homogeneous systems by Luttinger in 1961 [17] and it implies that the life time of a quasi-particle is inversely proportional to the square of its s.p. energy (referred to the Fermi energy) [108]. For the self-energy in finite systems such as in Eq. (3.103), the self-energy not only vanishes at just the Fermi energy, but also in a region around the fermi energy; this is the particle-hole gap mentioned in chapter 2. However, from Figs. 3.10 and 3.11 we see that the limited resolution introduced
Figure 3.10: Imaginary (upper diagram) and real (lower diagram) part of the second-order self-energy for the 3p orbital in argon. The dashed lines are the forward terms, the dash-dotted lines are the backward terms and the full lines are the sum of forward and backward contributions.

by the Lorentz-distributions cause a deviation from this rule.

It is clear from the figures that the extrema of the forward and backward imaginary parts respectively correspond to inflection points in the forward and backward real parts of the self-energy and *vice versa*. For 3p, forward and backward real part superimpose to a rather complicated form (backward and forward peaks are comparable in strength). In the case of 4s, it is observed that the forward peak (dashed line) is dominant. The dominance of the forward peak is also observed in studies of short-range correlations in nuclear matter when realistic nucleon-nucleon interactions are used and for densities around the nuclear-matter saturation density ($\rho_0 = 0.17 fm^{-3}$) [106]. Some typical results of these calculations are illustrated in Fig. 3.12. In this figure, forward and backward part of the imaginary and real part of the self-energy are displayed for nuclear matter with two different magnitudes of the wave vector, namely $k = 0.8 \times k_F$, to be compared with Fig. 3.10 and $k = 1.7 \times k_F$, to be compared with Fig. 3.11, where $k_F$ is the magnitude of the Fermi wave vector.
3.6. Results.

![Graphs of imaginary and real parts of the second-order self-energy for the 4s orbital in argon. See also caption of Fig. 3.10.](image)

Figure 3.11: Imaginary (upper diagram) and real (lower diagram) part of the second-order self-energy for the 4s orbital in argon. See also caption of Fig. 3.10.

(in the figures, a value of $k_F = 1.45 \text{fm}^{-1}$ is taken). The backward (forward) part of the real part of the self-energy, i.e. the lower left (right) panel of Fig. 3.12, is determined using the first (second) term in Eq. (3.104). Note that in a continuous system like nuclear matter we do not need to replace $\delta$ distributions by Lorentzian functions to obtain a smooth plot (as was done for Figs. 3.10 and 3.11). The backward (forward) part of the imaginary part of the self-energy vanishes for energies above (below) the Fermi energy [see left and right panels of Fig. 3.12]. For both wave vectors ($k = 0.8 \times k_F$ and $k = 1.7 \times k_F$), we clearly see that the forward part dominates (note the different scale between backward and forward part in the figure). The dominance of the forward part (for densities near the saturation density) indicates that the influence of (2p1h), (3p2h), ... on the real part of the self-energy is far larger than of (2h1p), (3h2p), ...: contributions from the backward part of the spectrum are perturbations of the self-energy generated by the forward part. We also focus the attention on the fact that in this figure, we do not use natural units.

Returning to Figs. 3.10 and 3.11, we note that the intricate behavior of the self-energy around the Fermi energy for $3p$ has important implications for the ionization energy. Depending on the detailed superposition of forward and backward terms
in the real part of the self-energy, the ionization energy can increase or decrease compared to the HF estimate. It is obvious that the two attractive minima of the real part of the self-energy around the Fermi energy in Fig. 3.10 try to draw the 3p level closer. From Table 3.9, it is found that the minimum just above the Fermi energy has the upper hand for argon: the ionization energy is less in Dyson(2) than in Dyson(1). Note that this is somewhat contrary to what could be expected from Fig. 3.4. This figure is actually a schematic image of the real part of the self-energy, when the δ-distributions in the self-energy are not replaced by Lorentz-distributions. There, the graphical solution is shown for a particle state and we concluded that the s.p. energy in Dyson(2) should be closer to the Fermi level. For a hole state, the same effect is expected. Yet, the self-energy graph can shift up or down depending on the precise combination of particle and hole contribution to the real part of the self-energy. In this way, there is no general rule to be derived about how the ionization energy will evolve from Dyson(1) to Dyson(2).

Now that we have arrived at the end of this chapter, it is good to give a summary...
of the most important topics covered. We have explained how the Dyson equation can be solved in a self-consistent way up to second order in the interaction for closed-shell nonrelativistic atomic systems. In the scheme, no relativistic or screening effects are considered and the Green’s function is assumed to be diagonal. We discussed the most important s.p. properties and conclude that the correlations embedded in the second-order term of the self-energy series are quite important to reach agreement with experimental data. In the next chapter, the extension to the open-shell case will be discussed.
Chapter 4

Self-consistent solution of Dyson’s equation: open-shell atoms.

4.1 Introduction.

This chapter is mainly based on the technology developed in the previous one: here we will concentrate on the typical problems that occur when dealing with Dyson’s equation for open-shell systems. The extension is not trivial, due to the loss of spherical symmetry because of the partially occupied shells, but can be simplified by applying an appropriate angular-averaging procedure.

In this chapter, we will study more in particular the second row of the Periodic System: B, C, N, O, and F. Due to the open-shell, a multi-configurational approach is mostly advisory (more than in the closed-shell case) to obtain valuable results (see e.g. [109]). For these systems a nonrelativistic approach is still acceptable but, contrary to the closed-shell atoms, the spins and angular momenta couple to nonzero orbital angular momentum $L$, spin $S$ and total angular momentum $J$. In this work we give preference to using an uncoupled representation, because in this way the formalism as developed for the closed-shell case remains essentially unchanged, after performing a suitable angular average. As stressed in the previous chapter, we did not take into account screening effects higher than second order. These higher-order effects are e.g. generated by ring or ladder diagrams in the self-energy and can be incorporated in the self-consistent scheme. However, this complicates the proposed algorithm substantially and is therefore out of the scope of this work.

This chapter will only dwell on the necessary adaptations of the closed-shell algorithm and on the predictions made by the extended scheme. Results for the total
binding energy, ionization energy and single-particle levels are discussed in detail and compared with the prediction of other computational tools and with experiment. In open-valence-shell atoms, a new quantity -the electron affinity- appears which was not relevant in closed-shell atoms. The electron affinities are very sensitive to the treatment of electron correlations, and their theoretical estimate is a stringent test for the adequacy of the applied scheme. The theoretical predictions are in good agreement with experiment. Also, the Dyson(2) scheme confirms the nonexistence of a stable negative ion of N. Similarly as in the closed-shell case, the overall effect of the self-consistent Dyson(2) scheme with regard to the Dyson(1) (i.e. Hartree-Fock) concept, is a systematic shift of all quantities, bringing them closer to the experimental values. The second-order effects turn out to be indispensable for a reasonable reproduction of the electron affinity.

Finally, we note that the problem of solving the Hartree-Fock equations in coordinate space (the first step in our algorithm), has also been addressed in refs. [47] and [48]. In this approach, however, the spin degrees of freedom are not taken into account, contrary to the approach which will be discussed in this chapter. As will become obvious in the discussion of the results, the inclusion of the spin leads to noticeable differences in e.g. the total energy.

4.2 Extended formalism and numerical scheme.

In this section, we give a short overview of the algorithm to solve Dyson’s equation self-consistently up to second order, and point out the extensions that are needed in open-shell systems. A more thorough discussion of the theoretical framework used in the Dyson(2) scheme can be found in chapter 2 and details on the Dyson(2) scheme itself were presented in chapter 3. Atomic units are used throughout.

4.2.1 Mean-field procedure and angular averaging.

First we address the impact of the open-shell features on the single-particle (s.p.) basis. In the previous chapter, a series of spin-saturated closed-shell atoms was treated nonrelativistically and without spin-orbit interaction. Using a spherical basis set with quantum numbers \( \alpha = (n_a, l_a, m_{l_a}, m_{s_a}) \), only the principal and orbital angular momentum quantum numbers \( (n_a, l_a) \) differentiated the radial wave functions, and the orbitals showed a degeneracy of \( 2(2l_a + 1) \) in the values \( (m_{l_a}, m_{s_a}) \) for the projection of orbital angular momentum and spin.

The extension presented here deals with the atoms B, C, N, O and F, open-shell atoms having a partially filled \( 2p \) orbital. If the angular and spin part of the spherical s.p. basis is retained,

\[
\varphi_\alpha(r, s) = \frac{1}{r} P_\alpha(r) Y_{l_a} m_{l_a} (\Omega) \chi_{m_{s_a}} (s),
\]  

(4.1)
the Hartree-Fock (HF) equations \((-\nabla^2/2 - Z/r - \epsilon_\alpha + \tilde{V}_H)\varphi_\alpha(r, s) = 0\), after integrating out the angular and spin dependence, become

\[
\left(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{l(l + 1)}{r^2} - \frac{Z}{r} - \epsilon_\alpha^{HF}\right) P_\alpha(r) + \sum_{\beta(\text{occ.})} \int dr' D_{\alpha\beta}(r, r') P_\beta(r')^2 P_\alpha(r) \\
- \sum_{\beta(\text{occ.})} \delta_{m_\alpha m_\beta} \int dr' E_{\alpha\beta}(r, r') P_\beta(r') P_\alpha(r) = 0. \tag{4.2}
\]

The radial wave functions \(P_\alpha(r)\) are normalized as \(\int dr P_\alpha(r) P_\beta(r) = \delta_{\alpha\beta}\). The summation over \(\beta\) includes only the s.p. states that are occupied in the HF ground state. The direct and exchange contributions to the HF potential read

\[
D_{\alpha\beta}(r, r') = \sum_{LM} \sum_{L' M'} \frac{4\pi}{2L+1} \langle l_b m_b | Y_{LM} | l_a m_a \rangle \langle l_b m_b | Y_{L'M'} | l_a m_a \rangle
\]

\[
E_{\alpha\beta}(r, r') = \sum_{LM} \sum_{L' M'} \frac{4\pi}{2L+1} \langle l_b m_b | Y_{LM} | l_a m_a \rangle \langle l_b m_b | Y_{L'M'} | l_a m_a \rangle
\]

\[
\text{where} \quad \langle l_b m_b | Y_{LM} | l_a m_a \rangle = \int d\Omega \ Y_{LM}^* (\Omega) Y_{L'M'} (\Omega). \tag{4.3}
\]

The HF equations (4.2) depend on the choice of the occupied \(m_{l_a}\) quantum numbers within the \(2p\) \(m_{s_a}\) orbital except for the nitrogen atom where, following the rule of Hund (see e.g. [12]), we assume full occupation of the \(2p\) orbital of one spin type. As a consequence, the radial wave functions and s.p. energies depend on \((m_{l_a}, m_{s_a})\) as well as on \((n_a, I_a)\). Keeping track of the full set of spherical quantum numbers would become unmanageable in the subsequent self-consistent Green’s function calculation, and we therefore introduce, in case of B, C, O, and F atoms, the following angular-averaging procedure (for the N atom no angular averaging is required):

(i) The \(l \neq 1\) orbitals are all fully occupied or completely empty. For these levels we perform a spherical averaging by summing in Eq. (4.3) over all substates \(m_l\) and dividing by the degeneracy \(2l + 1\). These orbitals are described by radial wave functions \(P_\alpha(r)\) characterized by the quantum numbers \(n_a, I_a, m_{s_a}\), independent of \(m_{l_a}\).

(ii) For the \(l = 1\) orbitals the angular averaging is somewhat more complicated due to the presence of a partially filled \(2p\) spin orbital, and should be performed in such a way as to prevent self-interaction in the HF mean field for the \(2p\) occupied states. The basic idea is to reduce the number of radial wave functions corresponding to different \(m_l\) quantum numbers, and limit the representation of the \(l = 1\) spinspace to two types of radial wave functions, one associated with the occupied \(2p\) \(m_{s_a}\) subspace (denoted \(\kappa = 1\)), and one associated with the unoccupied \(2p\) \(m_{s_a}\) subspace (denoted \(\kappa = 0\)). In this way the \(l = 1\)
spin orbitals are characterized by quantum numbers \( a = (n_{\alpha}, l_{\alpha} = 1, m_s, \kappa_a) \), independent of \( m_{l_a} \). The corresponding degeneracy \( d_a \) depends on the partial filling \( n_p \) of the 2p spin orbital with one or two electrons: \( n_p = 1 \) for the B and O atoms, and \( n_p = 2 \) for the C and F atoms. For \( l_a = 1 \) we thus have \( d_a = n_p \) for \( \kappa_a = 1 \) and \( d_a = 3 - n_p \) for \( \kappa_a = 0 \). For clarity the scheme is visualized in Fig. 4.1.

![Diagram of 2p spin orbital](image)

**Atoms: B and O**
- Occupied orbitals (\(-1\))
  - \( n_p = 1; d = 1 \)
- Unoccupied orbitals (\(-0\))
  - \( n_b = 3 - n_p = 2; d = 2 \)

**Atoms: C and F**
- Occupied orbitals (\(-1\))
  - \( n_p = 2; d = 2 \)
- Unoccupied orbitals (\(-0\))
  - \( n_b = 3 - n_p = 1; d = 1 \)

Figure 4.1: Partially filled 2p spin orbital in the open-shell atoms B, C, O, and F. For B and C, we choose the spin-up orbital to be partially occupied while the spin-up orbital is fully empty. For O and F, the spin-down orbital is fully occupied, while the spin-up is partially occupied (for clarity only the O and F case is illustrated in the figure). As in the text, \( n_p \) denotes the number of electrons in the partially filled spin orbital, while \( d \) stands for the degeneracy of the orbital characterized by quantum numbers \( (n, l, m_s, \kappa) \).

The procedure described above leads to the following averaged HF potential:

\[
\bar{D}_{ab}(r, r') = \frac{1}{(2l_a + 1)(2l_b + 1)} \sum_{m_{l_a} m_{l_b}} D_{\alpha \beta}(r, r')
\]

(4.5)

when at least one of \( l_a \) or \( l_b \) differs from 1;

\[
\bar{D}_{ab}(r, r') = \frac{1}{3} \sum_{m_{l_a} m_{l_b}} D_{\alpha \beta}(r, r') \delta_{m_{l_a} m_{l_b}}
\]

(4.6)
for \( l_a = l_b = 1 \) and \( d_a = d_b = 1; \)

\[
\tilde{D}_{ab}(r, r') = \frac{1}{12} \sum_{m_{t_a}m_{t_b}} D_{\alpha\beta}(r, r')(1 + \delta_{m_t m_{t'}}) \tag{4.7}
\]

for \( l_a = l_b = 1 \) and \( d_a = d_b = 2; \) and

\[
\tilde{D}_{ab}(r, r') = \frac{1}{6} \sum_{m_{t_a}m_{t_b}} D_{\alpha\beta}(r, r')(1 - \delta_{m_t m_{t'}}) \tag{4.8}
\]

for \( l_a = l_b = 1 \) and \( d_a = 1 \) and \( d_b = 2 \) (or \( d_a = 2 \) and \( d_b = 1 \)). The same expressions hold for the exchange part \( \tilde{E}_{ab}(r, r') \) of the HF potential.

In a more compact notation, which will be used in the remainder of the chapter, the angular averaged HF potential is rewritten as,

\[
\tilde{D}_{ab}(r, r') = \frac{1}{3} \sum_{\mu} \frac{1}{d_a d_b} \sum_{m_{t_a}m_{t_b}} w_{\alpha\mu} w_{\beta\mu} D_{\alpha\beta}(r, r'),
\]

\[
\tilde{E}_{ab}(r, r') = \frac{1}{3} \sum_{\mu} \frac{1}{d_a d_b} \sum_{m_{t_a}m_{t_b}} w_{\alpha\mu} w_{\beta\mu} E_{\alpha\beta}(r, r'),
\tag{4.9}
\]

where the summation over \( m_{t_a} \) and \( m_{t_b} \) is restricted by the \( w_{\alpha\mu} \) and \( w_{\beta\mu} \) coefficients according to

\[
\left\{ \begin{array}{ll}
  l_a \neq 1 & : w_{\alpha\mu} = 1 \\
  l_a = 1, \ d_a = 2 & : w_{\alpha\mu} = 1 - \delta_{m_{t_a}m_{t'}} \\
  l_a = 1, \ d_a = 1 & : w_{\alpha\mu} = \delta_{m_{t_a}m_{t'}}. \\
\end{array} \right.
\tag{4.10}
\]

In Eq. (4.9) the factor 1/3 and summation over \( \mu = -1, 0, 1 \) correspond to the averaging over the choice of occupied \( m_l \) values in the \( p \) spin orbital mentioned above. The coefficients \( w_{\alpha\mu} \) in Eq. (4.10) automatically select the correct \( m_l \) values for each choice of \( \mu \).

The final HF equations in radial space (for occupied as well as unoccupied states) read

\[
\left( -\frac{1}{2} \frac{d^2}{dr^2} - \frac{l_a(l_a + 1)}{r^2} - \frac{Z}{r} - \epsilon_{HF}^a \right) P_a(r) + \sum_{b(\text{occ.})} d_b \int dr' \tilde{D}_{ab}(r, r') P_b(r')^2 P_a(r) \\
- \sum_{b(\text{occ.})} d_b \delta_{m_{t_a}m_{t_b}} \int dr' \tilde{E}_{ab}(r, r') P_b(r') P_a(r') P_b(r) = 0.
\tag{4.11}
\]

In summary, we allow different spin orbitals for the two spin species. The angular-averaging procedure results, for \( m_s = \pm \frac{1}{2} \), in a single HF hamiltonian for each \( l \neq 1 \), and two HF hamiltonians corresponding to \( \kappa = 0 \) and \( \kappa = 1 \) in the \( l = 1 \) case. The construction of a complete and orthonormal set of s.p. states is then straightforward. Compared to the closed-shell case in the previous chapter,
the number of s.p. states is more than doubled, with a corresponding increase in the numerical effort. Therefore, a multi-threaded approach was implemented for the open-shell case: the set of orbitals was divided into two separate groups and the Dyson equation was solved for the two subsets in a simultaneous and parallel way, allowing for a more efficient use of present-day computer architecture.

4.2.2 Discussion on the averaging scheme.

Let us have an in-depth look at the averaging scheme for a practical case, namely fluor.

The summation index \( \mu \) in Eq. (4.9) actually has a physical background. As discussed in the previous subsection, we discriminate between the \( l = 1 \) spin orbitals that are occupied (\( \kappa = 1 \)) and those that are not (\( \kappa = 0 \)). In the case of fluor, two of the three available \( m_l \) quantum numbers are occupied (say) the spin-up 2p orbital (the spin-down orbital is considered fully occupied). This implies that we describe the 2p spin-up and -down orbital with two wave functions each (corresponding to the two values of \( \kappa \)). This gives a more accurate description of the partially filled 2p spin-up orbital, and allows for a polarization of the fully-occupied 2p spin-down orbital. It is clear that the problem of dividing two electrons over three \( m_l \) quantum numbers is equivalent to the problem of putting one hole in a completely filled p-orbital. The \( m_l \) value that is chosen for the hole is kept track of by an index \( \mu \).

To cover the three possibilities, we perform a sum over \( \mu \). For a fixed label of the hole (i.e. fixed \( \mu \)), we know which \( m_l \) can be attributed to the wave function with \( \kappa = 1 \) and which to \( \kappa = 0 \). In Eq. (4.9) the degree of degeneracy is expressed by the weighting factor: it reflects the number of possibilities to distribute one hole over three possible labels (\( \kappa = 0 \), unoccupied orbital) or two particles over three possible labels (\( \kappa = 1 \), occupied case). In this way, we obtain for an \( l = 1 \) orbital in fluor:

\[
\kappa = 0: \quad w_{\alpha \mu} = \delta_{m_l \alpha \mu} \Rightarrow \sum_{m_l} w_{\alpha \mu} = 1 = d_{\alpha},
\]

\[
\kappa = 1: \quad w_{\alpha \mu} = 1 - \delta_{m_l \alpha \mu} \Rightarrow \sum_{m_l} w_{\alpha \mu} = 2 = d_{\alpha}.
\]

Due to orthonormality conditions, this partitioning scheme must be applied to all \( l = 1 \) spin orbitals. Now that the physical background of Eq. (4.9) is clear, it can also be seen very easily that this expression is equivalent to Eqs. (4.5)-(4.8) by writing out the configurations taken into account explicitly. A similar analysis can be carried out for the other atoms. One final remark concerns the coupling of the global angular momentum \( L \) and the global spin \( S \) to the total angular momentum \( J \). Since we do not take the \( L \cdot S \) coupling term into consideration in the hamiltonian, all possible total angular momenta \( J \) are degenerate.
By means of this averaging scheme, we can include the impact of a partially filled shell in the model, while the main code of the closed-shell systems can still be used: we only have to adapt the implementation for the averaging scheme. The extended scheme will be discussed in more detail in the next subsection.

4.2.3 Dyson(1) calculation and construction of the basis set.

We now discuss in detail the numerical procedure to construct the set of s.p. states which is used subsequently for the second-order calculation. As in the closed-shell case, the construction is such that it approaches an almost exact treatment in coordinate space.

As before, the HF equations (4.11) are first solved in coordinate space on a radial grid, in order to avoid the inaccuracies inherent to the use of a finite basis set (e.g. of Gauss-type orbitals). In this way, we obtain the occupied states and the HF mean field. To find the unoccupied states, necessary in the second-order scheme, we again infer a parabolic potential well in the HF scheme, at a relatively large distance from the atomic center:

$$U_i(r) = C_i\theta(r - R_i)(r - R_i)^2.$$  \hspace{1cm} (4.13)

The values of the two parameters characterizing the parabolic potential are always chosen such that they do not affect the HF results for the occupied states (in other words that they coincide to high accuracy with the exact HF results without the wall). The precise method for choosing the wall parameters is discussed in the previous chapter, and involves an optimum speed of convergence of the second-order results in terms of the number of virtual orbitals. In section 4.2.5, evidence is provided in the case of carbon that the constructed basis set and the wall parameters ensure for an adequate accuracy of the results. In Table 4.1 the values of the parameters $C_i$ and $R_i$ we used are listed, along with the selected basis sets for the atoms.

Both occupied and unoccupied orbitals (which are now bound due to the wall in the modified scheme) are constructed in coordinate space, as eigenfunctions of the exact HF hamiltonian with the parabolic potential added. The eigenfunctions form a complete and orthonormal set, but a truncation of the basis set is needed for practical purposes. However, the truncation is done in a controlled manner, which does not affect the final results. We also refer to the previous chapter for a detailed discussion of this procedure. It turns out that about 130 to 180 orbitals are required to get sufficient convergence in the open-shell case.

At this point we have a discrete and finite basis set. The Dyson(1) calculation amounts to diagonalizing, within this basis set, the HF hamiltonian matrix without the confining parabolic potential. Of course, it is checked that the s.p. energies of the occupied states still correspond almost exactly to the original coordinate-space HF results obtained in the first self-consistent solution of the genuine HF equations.
Table 4.1: Values in atomic units for the parameters \( R_l \) and \( C_l \) of the parabolic potential \([\text{see Eq.(4.13)}]\), and number of radial wave functions retained in the discretization of the continuum. Between square brackets, the spectroscopic notation of the ground state of the atom is given.

<table>
<thead>
<tr>
<th>( l = 0 )</th>
<th>( R_l; C_l )</th>
<th>( B ,[^2P_{1/2}] )</th>
<th>( C ,[^2P_0] )</th>
<th>( N ,[^4S_{3/2}] )</th>
<th>( O ,[^2P_2] )</th>
<th>( F ,[^2P_{3/2}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( l = 1 )</td>
<td>( R_l; C_l )</td>
<td>( 7.7; 5.0 )</td>
<td>( 6.0; 5.0 )</td>
<td>( 5.0; 5.0 )</td>
<td>( 3.8; 5.0 )</td>
<td>( 3.5; 5.0 )</td>
</tr>
<tr>
<td>( l = 1 )</td>
<td>( l = 2 )</td>
<td>( l = 3 )</td>
<td>( l = 4 )</td>
<td>( l = 5 )</td>
<td>( l = 6 )</td>
<td>( l = 7 )</td>
</tr>
<tr>
<td>( l = 1 )</td>
<td>( l = 2 )</td>
<td>( l = 3 )</td>
<td>( l = 4 )</td>
<td>( l = 5 )</td>
<td>( l = 6 )</td>
<td>( l = 7 )</td>
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<td>( l = 1 )</td>
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<tr>
<td>( l = 1 )</td>
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<td>( l = 3 )</td>
<td>( l = 4 )</td>
<td>( l = 5 )</td>
<td>( l = 6 )</td>
<td>( l = 7 )</td>
</tr>
</tbody>
</table>

(i.e. without wall). The discrete HF basis obtained in this way is then used as the starting point of the self-consistent Dyson(2) calculation.

4.2.4 Dyson(2) calculation.

As usual, we will assume the s.p. propagator and the corresponding self-energy to be diagonal in the discrete HF basis obtained in the Dyson(1) scheme. In the previous chapter, it was clear that nondiagonal contributions could only occur between s.p. states differing exclusively in their principal quantum number. For the present treatment of open-shell systems in the uncoupled representation a similar statement can be made on the same grounds of conservation of the projection of total angular momentum and spin as in the closed-shell case. Note that the angular-averaging scheme as introduced in subsection 4.2.1 in its turn does not even permit mixing between states which differ only in the principal quantum number \( n \) and the additional label \( \kappa \). For instance, an electron belonging to \( 2p(\kappa = 1) \), can impossibly
be excited to a $5p(\kappa = 0)$ state, since this would evidently induce an imbalance in the averaging scheme and consequently violate the conservation of the projection $M$ of the total angular momentum. The electron can, of course, be excited to the $5p(\kappa = 1)$ level.

In general the energy separation between orbitals with the same principal quantum number $n$ is large enough to reduce inter-shell mixing, though in the open-shell case this reasoning becomes questionable for the discretized continuum states. Indeed, the level determining the electron affinity is most prone to inter-shell mixing. However, as will be discussed in section 4.3, the results for this observable are in fairly good agreement with experiment, indicating that these effects are certainly not dominant. It should also be stressed again that the assumption of diagonality in the principal quantum number is not strictly necessary, but serves to make the equations more tractable and to decrease the numerical effort.

Using the s.p. labels $a$ as introduced in subsection 4.2.1, the spectral representation of the Green’s function can be written as the following sum,

$$
G_a(E) = \sum_j \frac{S^f_{a,j}}{E - \epsilon^f_{a,j} + i\eta} + \sum_j \frac{S^b_{a,j}}{E - \epsilon^b_{a,j} - i\eta}.
$$

(4.14)

The coefficients $S^f_{a,j}$ and $S^b_{a,j}$ in Eq. (4.14) are defined as [compare with Eq. (3.44)].

$$
S^f_{a,j} = |\langle j(A + 1)_{a} | c^f_{a} | 0(A) \rangle|^2, \quad S^b_{a,j} = |\langle j(A - 1)_{a} | c_{a} | 0(A) \rangle|^2
$$

(4.15)

and represent the spectroscopic strength for respectively the addition and removal of an electron in spin orbital $a$ of the correlated $A$-electron ground state $|0(A)\rangle$. The summation index $j$ is restricted to the $(A \pm 1)$-electron states that can be reached from the ground state by adding or removing an electron in spin orbital $a$. The corresponding energies of these $(A \pm 1)$-electron states are related to the poles $\epsilon^f_{a,j}$ and $\epsilon^b_{a,j}$ in Eq. (4.14) as [see Eq. (2.18)]

$$
\epsilon^f_{a,j} = \langle j(A + 1)_{a} | H | j(A + 1)_{a} \rangle - E_{0(A)},
\epsilon^b_{a,j} = E_{0(A)} - \langle j(A - 1)_{a} | H | j(A - 1)_{a} \rangle.
$$

(4.16)

The spectroscopic strengths are a measure for the fragmentation of spin orbital $a$ over the states of the $(A \pm 1)$ system due to correlations. In the HF approximation, the Green’s function $G^{(1)}_a(E)$ has only one pole, corresponding to the HF energy $\epsilon^H_{a}$ of spin orbital $a$, with the corresponding spectroscopic strength equal to unity. The resulting expression is:

$$
G^{(1)}_a(E) = \frac{\theta(\epsilon^H_{a} - \epsilon^F)}{E - \epsilon^H_{a} + i\eta} + \frac{\theta(\epsilon^F - \epsilon^H_{a})}{E - \epsilon^H_{a} - i\eta},
$$

(4.17)
where $\epsilon_F$ is again the Fermi energy of the system (i.e. the average of the highest occupied and lowest unoccupied HF state).

In a self-consistent formulation, the dressed propagators of Eq. (4.14) should be used to evaluate the electron self-energy. The contribution to the self-energy of second order in the interaction then reads

$$
\Sigma^{(2)}_a(E) = \sum_{b,c,d} \frac{1}{2d_{a}} \sum_{j,k,l} \left\{ \frac{S^f_{c,j} S^f_{d,k} S^b_{l,j}}{E - (\epsilon^f_{c,j} + \epsilon^f_{d,k} - \epsilon^b_{l,j}) + i\eta} + \frac{S^b_{c,j} S^b_{d,k} S^f_{l,j}}{E - (\epsilon^b_{c,j} + \epsilon^b_{d,k} - \epsilon^f_{l,j}) - i\eta} \right\}.
$$

The interaction coefficients $F_{ab,cd}$ in Eq. (4.18) are angular-momentum averaged in case of a partially filled $np$ shell, consistently with the procedure used for the mean field in Eqs. (4.9-4.10). The general expression in terms of (antisymmetrized) matrix elements of the Coulomb interaction $W$ reads

$$
F_{ab,cd} = \frac{1}{3} \sum_{\mu} \sum_{m_{l\mu},m_{l\mu},m_{l\mu},m_{l\mu}} w_{\mu m_{l\mu}} w_{\mu m_{l\mu}} w_{\mu m_{l\mu}} w_{\mu m_{l\mu}} | \langle (am_{l\mu})(bm_{l\mu}) | W | (cm_{l\mu})(dm_{l\mu}) \rangle_{as} |^2,
$$

where the summation over $\mu = -1,0,1$ represents the averaging over the occupied $m_l$ values in the $np$ shell.

The self-consistent solution is then found by the following iteration process

$$
G^{(n+1)}_a(E) = \frac{1}{E - \epsilon^H a} - \Sigma^{(n)}_a(E) \quad \text{(4.20)}
$$

$$
= \sum_j \frac{S^{[n+1]}_{a,j}}{E - \epsilon^{[n+1]}_{a,j} + i\eta} + \sum_j \frac{S^{[n]}_{a,j}}{E - \epsilon^{[n]}_{a,j} - i\eta}. \quad \text{(4.21)}
$$

The HF propagator in Eq. (4.17) is used as the starting point ($n = 0$) of the iterative scheme.

The second-order self-energy in iteration $n$, $\Sigma^{(2)}_a(E)$, is constructed with the propagator of iteration $n$, i.e. Eq. (4.18) is evaluated with $S^{[n]}_{a,j}$, $\epsilon^{[n]}_{a,j}$, $S^{[n]}_{a,j}$, and $\epsilon^{[n]}_{a,j}$, representing the fragmented distribution of poles and spectroscopic strength in iteration step $n$. Also the first-order contribution $\Sigma^{(1)}$ to the self-energy must be evaluated with the dressed Green's function, resulting in HF-like energies which are updated in each iteration step as

$$
\epsilon^H a = \langle a | H_0 | a \rangle + \frac{1}{d_{a}} \sum_{\mu} \sum_{c,m_{l\mu}} w_{\mu m_{l\mu}} w_{\mu m_{l\mu}} \langle (am_{l\mu})(cm_{l\mu}) | W | (am_{l\mu})(cm_{l\mu}) \rangle_{as} \sum_j S^{[n]}_{c,j}.
$$

(4.22)
where $H_0$ is the one-body part (kinetic energy and nuclear Coulomb field) of the hamiltonian.

As in the closed-shell case, the BAGEL scheme is adopted to reduce the increasing number of poles in the self-energy during successive iterations. In each iteration step the poles and residues in the self-energy are replaced by a fixed (smaller) set of BAGEL poles, determined by the requirement that the lowest-order energy-weighted moments are equal for the genuine and the BAGEL distributions. For a sufficiently large number of BAGEL poles, this replacement has no influence on the distribution of spectroscopic strength near the Fermi energy, nor on the total binding energy. Note that the total binding energy in the Dyson(2) scheme can be calculated (see previous chapter) using the Migdal-Galitskii expression

$$E_{gs}(A) = \frac{1}{2} \sum_{a_j} \left( \langle a \mid H_0 \mid a \rangle + \epsilon_{a,j}^b \right) S_{a,j}^c,$$  \hspace{1cm} (4.23)

and is seen to depend only on the zeroth and first energy-weighted moment of the backward distribution of spectroscopic strength. Of course, in the sum over the s.p. orbitals we have to take into account the averaging scheme as well. The moment reproduction for the self-energy then ensures a fast convergence also for the total binding energy, as will become evident from the results in the next section. About 20 BAGEL poles are required to reach a satisfactory reproduction of the genuine distribution, i.e., taking a larger number of poles has no significant effect on the binding energy and valence ionization energy or electron affinity. A more thorough discussion of the BAGEL algorithm can be found in the previous chapter.

### 4.2.5 Choice of basis set and parameters: case study for carbon.

In this section we illustrate how several parameters that enter the calculation, such as the confining potential, the number of virtual orbitals, and the number of BAGEL poles were chosen. We use the calculation for the carbon atom as an example.

As in the closed-shell algorithm, the number of virtual orbitals was decided by considering the ionization energy $I_1$ in the first iteration, i.e., using the HF propagators to evaluate the second-order self-energy and solving the corresponding Dyson equation for the highest occupied HF level. All two-hole/one-particle and two-particle/one-hole intermediate states are taken into account in the second-order self-energy: the BAGEL approximation was not yet used at this level. Table 4.2 contains the ionization energy for a test calculation where only $s$ and $p$ orbitals are considered, for an increasing number of virtual orbitals, and for three quite different parabolic potentials [see Eq. (4.13)]. Again, the value of $C_l = 5$ is taken constant, but the parameter $R_l$, which determines the position of the wall, is taken as $R_l = 3$, $R_l = 6$, and $R_l = 10$ a.u., respectively.

It is clear from Table 4.2 that the ionization energy also converges in the open-shell case to the same value for all choices of the parabolic potential, provided that
Table 4.2: Carbon first ionization energy (atomic units). Results obtained using the second-order self-energy in the first iteration (see text). Only s and p orbitals were considered. The parameters of the parabolic potential are $C_l = 5$, and $R_l = 3$ (top), $R_l = 6$ (middle), $R_l = 10$ (bottom). $N_s$: number of s-orbitals, increasing with row number. $N_p$: number of p-orbitals, increasing with column number.

<table>
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<th>$N_s$</th>
<th>$N_p$</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
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<tr>
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<td>0.3964</td>
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<tr>
<td></td>
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<td>0.3964</td>
<td>0.3964</td>
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<td>0.3965</td>
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<tr>
<td></td>
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<td>0.3965</td>
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</tr>
</tbody>
</table>

enough virtual orbitals are taken into account. However, the convergence is fastest using the parabolic potential with $R_l = 6$ atomic units. This is understood by realizing that for a small value of the wall distance $R_l$ the confining potential distorts the HF potential and hence the bound orbitals. It then requires a large number of virtual orbitals to get back to the coordinate-space HF wave functions and energies. On the other hand, for a very large value of $R_l$ the level spacing of the virtual orbitals becomes quite small. In this case a large number of virtual orbitals are needed to provide a cut-off in energy which is sufficient to reach convergence for the second-order diagram. The same holds true if the curvature $C_l$ of the parabolic potential is made very small instead of the position $R_l$ very large. Stated differently, there exists an optimal value for the parameters of the confining potential, which allows for an accurate discretization of the HF continuum in terms of a limited set of virtual orbitals, and leads to fast convergence of the second-order self-energy in terms of the energy range covered in the continuum.

The parameter values of the confining potential which are listed in Table 4.1 were determined by a great number of test calculations like the one described above, involving first the $l$-values corresponding to the occupied HF states, and in a second
stage the higher $l$-values. In all cases we checked convergence for the first ionization energy, up to approximately $10^{-4}$ a.u. by gradually increasing the number of virtual orbitals. Then we determined the parameter $R_i$ for which convergence was optimal in terms of the number of virtual orbitals. The value of $C_i$ was kept fixed at $C_i = 5$ a.u. which we found to be a reasonable value in all calculations. Note that inclusion of angular momenta with $l \geq 8$ did not affect the ionization energy $I_1$ up to the required accuracy. This procedure resulted in the basis sets that were already presented in Table 4.1. At this point we have converged results, in terms of the basis-set dimension, for the second-order diagram evaluated with HF propagators, i.e., the first iteration result in our iterative scheme towards the self-consistent solution. For the case of the carbon atom, e.g., we find a value of 0.4166 a.u. for the first-iteration ionization energy $I_1$.

As mentioned in subsection 4.2.4 and the previous chapter, the self-energy and the Green's function must be replaced by a BAGEL approximation containing a limited number of poles. We next investigated the dependence of the first-iteration ionization energy, as a function of the number of BAGEL poles $M$, by solving the Dyson equation with the self-energy in the corresponding BAGEL approximation. For $M = 10, 15, 20$ the result is, respectively, $I_1 = 0.4171, 0.4167, 0.4166$ atomic units. Note the convergence, with increasing number of poles, to the first-iteration result obtained without the BAGEL approximation. In our self-consistent calculations on the open-shell atoms, $M = 20$ BAGEL poles are taken into account. This is sufficient to guarantee converged results for the ionization energy, electron affinity, and total binding energy. For carbon we checked this explicitly by performing fully self-consistent calculations with $M = 10$ and $M = 15$ poles, additional to the standard calculation with $M = 20$ poles. For the carbon binding energy (in atomic units) we find $-37.790, -37.789, -37.789$ for $M = 10, 15, 20$ poles, respectively. This indicates the rapid convergence of the binding energy, which is essentially converged even at $M = 10$. The outcome for the ionization energy ($0.417, 0.416, 0.415$) behaves similarly, whereas the predictions for the electron affinity ($0.040, 0.045, 0.046$) are somewhat more sensitive in this respect.

4.3 Results.

In this section, we present the most important results of the Dyson(1) and Dyson(2) calculations on the second-row atoms B, C, N, O, and F. These open-shell atoms show near-degeneracy effects in the valence shell, and the presence of strongly interacting configurations [109] make a high-level treatment of electronic correlations mandatory. A comparison between theoretical results obtained in this work and those from computational schemes available in the GAUSSIAN 98 package [77] (standard HF, post-HF, DFT) is provided. Of course, where possible, we try to test the predictions to experiment. In the DFT calculations, two frequently used functionals
were applied (BLYP and B3LYP), while the standard HF calculations are performed on the HF/6-311g** level. The post-HF methods include electron correlations by means of different perturbation schemes such as Møller-Plesset perturbation theory (MP2, MP4) or configuration interaction (CI). As throughout this work, all results are denoted in atomic units.

First, we discuss some s.p. properties for the open-shell atoms. In Table 4.3 and Table 4.4 we report the prediction of the first ionization energies, respectively the electron affinities. These properties can be calculated in two distinct ways. One method is the so-called adiabatic or relaxation approach, where the atom and ion are optimized separately and the ground-state energies are subtracted subsequently. In this way, collective features such as relaxation of the orbitals are included and rearrangement effects in the mean field of the \((A \pm 1)\) system due to the removal or addition of an electron are taken into account. The present Green’s function treatment, on the other hand, is a perturbative expansion starting from the neutral atom. The energy poles of the exact Green’s function give simultaneously the excitation energies of the \((A \pm 1)\) electron system. The highest pole in the backward propagating part corresponds to the ionization energy which is in first order (HF approximation) represented by the HF s.p. energy of the highest occupied bound level. This approach does not take into account rearrangement effects directly, as in the adiabatic scheme.

Table 4.3: First ionization energies (in atomic units). Dyson(1) stands for HF in the discrete basis discussed in the text. Dyson(2) gives the solution of the second-order Dyson equation after one and two iterations and after convergence. Experimental data are taken from Ref. [110] (°), Ref. [111] (°), Ref. [112] (°), Ref. [113] (°), Ref. [114] (°).

<table>
<thead>
<tr>
<th></th>
<th>BLYP</th>
<th>BLYP</th>
<th>BLYP</th>
<th>BLYP</th>
<th>HF/6-311g**</th>
<th>Dyson(1)</th>
<th>Dyson(2)</th>
<th>Exp.</th>
</tr>
</thead>
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<td>B</td>
<td>0.318</td>
<td>0.741</td>
<td>0.148</td>
<td>0.187</td>
<td>0.317</td>
<td>0.311</td>
<td>0.308</td>
<td>0.308</td>
</tr>
<tr>
<td>C</td>
<td>0.417</td>
<td>0.424</td>
<td>0.211</td>
<td>0.264</td>
<td>0.437</td>
<td>0.430</td>
<td>0.417</td>
<td>0.415</td>
</tr>
<tr>
<td>N</td>
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<td>0.538</td>
<td>0.286</td>
<td>0.352</td>
<td>0.568</td>
<td>0.571</td>
<td>0.574</td>
<td>0.573</td>
</tr>
<tr>
<td>O</td>
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<td>0.516</td>
<td>0.336</td>
<td>0.374</td>
<td>0.516</td>
<td>0.510</td>
<td>0.490</td>
<td>0.494</td>
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<tr>
<td>F</td>
<td>0.645</td>
<td>0.647</td>
<td>0.323</td>
<td>0.431</td>
<td>0.670</td>
<td>0.674</td>
<td>0.688</td>
<td>0.691</td>
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</table>

First of all, we note that the adiabatic DFT results (first two numerical columns in Table 4.3) show a remarkable agreement with experiment, which emphasizes the semi-empirical nature of the DFT-functionals and the fact that these atoms were part of the training set for these functionals (see chapter 5). On the other hand, we observe from the third and fourth column of Table 4.3 that Koopmans’ theorem is not valid for Kohn-Sham (KS) levels as clearly demonstrated by the poor DFT results. In fact, as will be pointed out in chapters 5 and 6, the highest occupied KS level in the DFT scheme exactly equals the ionization energy in theory, but many approximate
DFT functionals fail in this respect. This is because in the fitting procedure of most approximate functionals only the area where the density is substantial has been taken into account properly. The asymptotic region, crucial for the ionization energy, is generally less important when constructing a DFT functional. As will be explained in chapter 5, the prediction of the ionization energy is also related to the constant shift we can add to the exchange-correlation potential. This will also be of some importance in chapter 6. The nonadiabatic HF estimates are reasonable, indicating that Koopmans' theorem is valid in HF approximation to some extent, but apparently insufficient correlations are involved to allow for a more stringent agreement. Anyway, Dyson(1) provides a good starting point for Dyson(2) and it is obvious that the correlations included in the self-consistent second-order scheme generally have a beneficial effect. To illustrate the convergence to self-consistency, results of the first and second iteration are given as well. It is observed that Dyson(1) overestimates the ionization energy for all open-shell atoms in this study and that the evolution toward convergence in Dyson(2) is mostly monotonous.

Table 4.4: Electron affinities (in atomic units). See also caption of Table 4.3. Experimental data from Ref. [115] (a), Ref. [116] (b), and Ref. [117] (c).

<table>
<thead>
<tr>
<th>DFT</th>
<th>CCSDT</th>
<th>HF</th>
<th>Dyson(2)</th>
<th>Expt.</th>
</tr>
</thead>
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<td></td>
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<td></td>
</tr>
<tr>
<td>H</td>
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<td>0.01047</td>
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<td>-0.0028</td>
</tr>
<tr>
<td>C</td>
<td>0.00145</td>
<td>0.0019</td>
<td>0.00041</td>
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</tr>
<tr>
<td>N</td>
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<td>-</td>
<td>-0.109</td>
</tr>
<tr>
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<td>0.05368</td>
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<td>0.0675</td>
<td>0.12065</td>
<td>-0.066</td>
</tr>
</tbody>
</table>

In Table 4.4 the results for the electron affinity are collected. This observable is known as one of the atomic properties that is hardest to reproduce in an \textit{ab initio} calculation. The electron affinity provides a useful test of the computational method because correlations are generally believed to be extremely important in this quantity. This holds in particular for boron which forms the most weakly bound \textit{stable} ion among the light elements [115], and has been the subject of many theoretical studies [119]-[124]. The negative ion of nitrogen has a long history as well: from the early experiment of Fogel' et al. [125] and the dissociative attachment experiment of Hotop et al. [126] up till now, no proof of the existence of this ion has been published. Computational estimates vary as well [127, 128]. The last two atoms (O and F) are known to have electron affinities that are of the most difficult ones to reproduce (see e.g. refs. [118, 121, 122, 129]). For O, the Dyson (2) result is noted to give only a moderate agreement with experiment, but for F, the prediction is quite accurate.

The fact that electron correlations play a dominant role in the electron affinity is clearly demonstrated by the HF results [Dyson(1)], which fail in reproducing even
the qualitative trend of the binding energies of the \((A+1)\)-system versus \(A\)-particle system, resulting in a negative affinity (i.e., no electron can be bound). The first two numerical columns of Table 4.4 give the electron affinities as obtained in DFT calculations using standard functionals. We also report coupled-cluster calculations (CCSDT) with inclusion of several correction terms [118]: the predicted theoretical values of this reference are of the best available in literature to the present day and are defined following an adiabatic approach: \(E_{0(A)} - E_{0(A+1)}\). Very large basis sets are used and various corrections such as extrapolation to the basis-set limit and relativistic effects have been considered. As a consequence, the results of Ref. [118] have an excellent agreement with experiment but lack the microscopic basis as offered e.g. in the Green’s function approach.

To demonstrate the fact that correlations (as implemented in DFT) are extremely important to reproduce a sensitive observable such as the electron affinity we also include in Table 4.4 adiabatic HF results using finite basis sets (HF/6-311g**). They are scarcely better than the Dyson(1) results (i.e., the lowest unoccupied HF s.p. energies in the discretized basis). No extra electron can be bound in the HF system (apart from the case of the highly electronegative fluor), and we conclude that both HF schemes completely fail in reproducing even the qualitative trend of the electron affinity throughout the second-row atomic systems in this study.

As opposed to HF, the Dyson(2) results turn out to be quite satisfactory. For most atoms the first iteration yields a dramatic change towards the experimental value, but the predicted figures for the electron affinity still vary significantly from the converged results. This supports the important role of the complex electron correlations generated by the “dressed” second-order self-energy. For boron it is noted that the second iteration is even indispensable to provide a binding orbital for an additional particle. For the nitrogen atom the electron affinity remains negative, in agreement with experiment where no stable negative nitrogen ion can be found. Of course the present calculation, being nonvariational in nature, cannot rule out the existence of a stable negative nitrogen ion. Moreover, for such a system on the verge of stability the description of the single-particle continuum is likely to be crucial. Nevertheless, all atoms start from the same type of HF spectrum, having no bound unoccupied \(p\) orbital, and it is satisfactory to see that the electron correlations in the Dyson(2) scheme pull down one \(p\) orbital to negative energies for all atoms in Table 4.4, except for nitrogen.

The final converged Dyson(2) results show good agreement with the experimental trend, and for carbon and fluor the predicted electron affinity is even remarkably accurate. In this respect, we emphasize again that the electron affinity derived in the Dyson(2) scheme represents a pole in the spectral representation of the neutral atom Green’s function, which simultaneously contains information on electron affinities and ionization energies. Within the Green’s function approach, the electron affinity is not determined from separate calculations of the ground-state energies of neutral atom and negative ion.
A summary of all s.p. energies is given in Table 4.5. In the case of O and F, we assume the 2p spin-down level to be fully occupied (in agreement with the averaging scheme of subsection 4.2.1, we present two s.p. energies for this level). For the other atoms, we chose the 2p spin-up level to be completely empty. In the case of the partially occupied level, only one of the two radial wave functions is occupied and therefore we report just this one in Table 4.5, the other one determines the electron affinity. The energies in the first two numerical columns are standard DFT and HF results obtained in finite basis sets using the GAUSSIAN 98 software package. The s.p. energies reported for DFT-B3LYP are Kohn-Sham energies and in principle of no physical significance, despite the apparent experimental agreement for the more deeply bound 1s level. The third column collects the HF energies from a computational scheme that also solves the HF equations in coordinate space [47]. This scheme solves the single-configuration HF equations, without distinguishing spins.

Table 4.5: Single-particle properties (energies in atomic units). Experimental data for core levels from Ref. [97]; for the valence levels see caption Table 4.3. HF(*) results are from Ref. [123].

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Finally the energies of both Dyson(1) and Dyson(2) schemes are reported in the next two columns. A thorough discussion has already been held for the valence ionization energies. For the core levels the experimental information is less accurate: experiments (using EMS, see previous chapter) on open-shell atoms are more involved than on closed-shell atoms and are generally limited to a rather narrow energy range. Therefore the experimental data for the \( l = 0 \) levels in Table 4.5 are deduced from experiments on solids. Since these levels are so tightly bound that they are relatively inert, we assume that their energies are more or less independent of the state of aggregation. The predictions for the core s.p. energies in the two HF schemes [HF/6-311g** and Dyson(1)] are alike. This is not surprising, since the benefits of a scheme in coordinate space are more apparent on the wave functions than on the energy. We conclude from the Table that the Dyson(2) scheme seems to make the core levels somewhat less bound, in agreement with experiment.

![Figure 4.2: Spectroscopic strength of 1s\(_\downarrow\) in oxygen as predicted in the Dyson(1) and Dyson(2) scheme.](image)

In Fig. 4.2 we demonstrate the fragmentation process of the 1s spin-down level of oxygen from Dyson(1) to the converged Dyson(2) result, as we did for neon in the closed-shell calculation. The same conclusions can be drawn as in Fig. 3.6: it is observed that the first iteration in the second-order procedure scatters the spectroscopic strength over a large energy range and that the correlations induce a shift of the quasi-particle energy towards the Fermi energy. The effect of self-consistency is mainly to recluster the strength into a few fragments and to further deplete the quasi-particle peak, while its energy varies only little.
Table 4.6 gives an overview of various predictions of the total ground-state energy for the open-shell systems. In the Dyson(2) scheme, the total energy can be calculated (for details, see previous chapter) as

\[
E_{\alpha A} = \frac{1}{2} \sum_{a=1}^{N_b} \sum_{j=1}^{N} S_{a j}^b \left( \langle a | H_0 | a \rangle + \epsilon_{a j}^b \right).
\]  

(4.24)

In this equation, \( N_b \) is the dimension of the basis set and \( N \) is the number of backward poles (as before, \( H_0 \) is the one-body part of the Hamiltonian). The DFT results are superior to those of the other schemes: the reason for this success has already been explained in the previous chapter.

Table 4.6: Total ground-state energy (atomic units) obtained with various many-body models. In MP4, calculations with double-quadruple (DQ), single-double-quadruple (SDQ), and single-double-triple-quadruple (SDTQ) substitutions in the ground-state Slater determinant are considered. Experimental data are from Ref. [88].

<table>
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<tr>
<td>Dyson(2)</td>
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<tr>
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<td>Expt.</td>
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<td>-37.844</td>
<td>-54.587</td>
<td>-75.063</td>
<td>-99.725</td>
</tr>
</tbody>
</table>

We include three HF calculations in Table 4.6. Their results are almost identical, though Dyson(1) unsurprisingly predicts a somewhat larger binding energy, since it stands for the exact HF solution in coordinate space. The other two schemes either suffer from finite-basis effects (HF/6-311g**) or do not adopt the spin degree of freedom in the calculation (Ref. [47]) which leads to a slightly less bound system.
To include gradually a larger amount of correlations in the description, we also consider post-HF results in Table 4.6 based upon application of perturbation techniques beyond HF, such as MP2, MP3 and a few MP4 schemes. Finally a variational approach such as configuration interaction (CI) calculation has been performed. When comparing these results with the Dyson(2) energies it should be kept in mind that the post-HF results were all performed using standard finite basis sets, which makes a quantitative comparison with Dyson(2) somewhat unfair. They are merely quoted to give an idea about the effect of gradually including a larger amount of correlations in the description. Compared to HF, all these calculations predict binding energies that are larger and closer to the experimental outcome. However, the electron correlations which become more and more involved in these perturbation models are not of the same complexity as those present in the Dyson(2) scheme. Even after the first iteration, we already predict a more stable atom than CI (except for boron), and this tendency persists till convergence.

4.4 Summary and conclusions.

So far, we have introduced the Green’s function formalism (chapter 2) and solved Dyson’s equation for closed- and open-shell atomic systems (chapters 3 and 4). It was explained that to tackle Dyson’s equation up to second order in the interaction, we first solve the HF equations in coordinate space. To allow for a numerical description of the continuum, a confining potential wall is added. The resulting discrete basis set is truncated in such a way that it offers a good description of the continuum and that it is complete for all practical purposes. Concerning the quantum labels needed to keep track of the eigenfunctions and eigenenergies, the principal quantum number $n$ and the orbital angular momentum $l$ suffice in the closed-shell case. In an open-shell context, a more involved set of quantum numbers is required, since the electrons in the system no longer couple to zero total angular momentum. The labeling scheme can however be simplified by means of angular-averaging of the spin orbitals. This ensures that only a few extensions of the closed-shell scheme are needed to apply it to open-shell atoms and that the equations can still be solved in the uncoupled representation.

We demonstrated that the dimensionality problem which occurs when solving the Dyson equation in second order, can be coped with using the BAGEL approach. In the discussion of the results we compared the Green’s function calculations with other computational schemes and with experiment. It became apparent that the correlations embedded in the second-order scheme entail a fair reproduction of the experimental value on account of the total energy, the ionization energy, and s.p. energy levels in general. For the open-shell atoms, the electron affinity proved to be a good testcase where we can see the effect of correlations at work. As indicated, the Dyson(2) scheme passes this test as well. In this respect, the scheme also confirms
the experimentally demonstrated instability of the anion of nitrogen.

The key advantage of the Green’s function formalism is that the nature of the included correlations can be identified by means of Feynman diagrams as was discussed thoroughly in chapter 2. In the presentation of the results of our calculations, it was mentioned that the only scheme able to rival the Dyson(2) method in predicting the total energy, is Density Functional Theory (DFT). We explained that this was due to the semi-empirical nature of the functionals used to implement the DFT scheme. In the next chapters, a survey of DFT will be given and it will become clear that the predictive power of DFT largely depends on the approximation to the exchange-correlation functional (a universal object which mimicks the interelectron interactions in a many-body system) that is used in the calculation. The problem is the lack of a detailed picture of what kind of interactions are included in present-day exchange-correlation functionals. Therefore, we intend to use the Dyson(2) calculations to learn more about the correlations which are implemented in functionals for DFT and find a microscopic basis for the exchange-correlation functional.

In this respect, the extension to open-shell systems is important to gain insight into the spin-dependent correlations. The microscopic approach presented in this and the previous chapter, can be employed to identify a “universal background” contribution to correlation effects in atomic systems. In this way, Green’s function calculations can shed new light on the correlations which are (to be) included in exchange-correlation functionals for use in DFT.
Chapter 5

Density Functional Theory

5.1 Basic principles of Density Functional Theory.

In this chapter, an overview is given of a many-body theory that is quite successful in describing complex systems: Density Functional Theory (DFT). Contrary to the Green’s function theory that was discussed so far, DFT is not a microscopic scheme but resorts to a phenomenological description of the many-body ensemble. This turns DFT into a computationally fast scheme, but the accuracy of its predictions largely depends on the quality of the phenomenological potential used to model the two-body interaction present in the system. Nevertheless, DFT extends with success the range of applications to problems that are at present totally beyond the capability of microscopic schemes. In particular, DFT can be used to study proteins, saccharides, periodic-structure calculations, catalytic reaction processes, and liquids.

Two key concepts of the DFT scheme explain this large applicability. First, the formalism focuses on finding the electron density without determining the many-body wave function. The former quantity depends only on three variables (the space coordinates), while the latter involves $3N$ (where $N$ is the number of particles in the system)! It is clear that when the number of electrons becomes large, an approach based on the total wave function cannot possibly be an option. Also, the electron density can be visualized very easily and is of direct physical importance. On the other hand, the question may arise how much information is lost when taking the electron density as central variable instead of the intricate many-body wave function. Most surprisingly, one of the founding theorems of DFT proves that there is a unique mapping of the many-body wave function on to the ground-state electron density and vice versa: in principle no information is lost.

The second concept in DFT is that all two-body interactions are modeled by means of a local and energy-independent one-body potential. As was obvious in
the discussion of the Dyson(1) and Dyson(2) scheme (see chapter 3), the numerical difficulties in solving the equations for the Green’s function are mainly due to the nonlocality of the Fock term in the Hartree-Fock Hamiltonian and the energy dependence of the second-order self-energy. Remind that this energy dependence was caused by the effort to fold the two-body interactions into a one-body formalism. Therefore, it may be surprising that this folding can actually be implemented using a local and energy-independent one-body potential. Here, the founding theorems of DFT again provide an answer: as we will see, the first theorem of DFT implies that there is a unique functional of the density that is the same for all many-body systems in which the particles interact via the Coulomb interaction. Only the external (one-body) potential differs between these systems (if we keep the number of electrons fixed) and gives the corresponding density its characteristic shape. Unfortunately, the theorems give no clue on how to construct the universal functional. Although there are functionals that have been derived on a fully \textit{ab initio} basis, present-day DFT calculations often use approximations that are deduced in a semi-empirical way (such as the popular BP86, BLYP, and B3LYP parametrizations). In the latter approach, some form for the functional is proposed starting from theoretical considerations. Generally, parameters are introduced in this form which are fitted to experimental data. This introduces a phenomenological nature into the DFT scheme. Practical calculations involve the solution of single-particle equations in which the derivative of the universal functional with respect to the density features. This functional derivative is a one-body potential. So far, only local and energy-independent potentials have been taken into serious consideration. Therefore, the practical implementation of DFT along with the large applicability and accuracy of the scheme point out that a good description of a many-electron system is indeed possible using a local and energy-independent one-body potential, contrary to what would be expected from the previous chapters of this work.

In this chapter, the principles of the Density Functional scheme are explained. First we will focus on the electron density which is the key observable of the formalism (section 5.2). Next, the basic theorems are discussed along with the practical implementation of DFT (sections 5.3 and 5.4). There it will become clear that every observable of a many-body system is actually a functional in the electron density. Finally, some important approximations to the universal functional will be studied, along with some theoretical conditions that the exact functional should obey (sections 5.5 and 5.6). A mathematical summary of the concept of functionals is provided in App. D. As in the case of the Green’s function formalism, we will only cover the topics of DFT that are of relevance to this work. A more thorough analysis of DFT can be found in the standard references [103], [130], and [131]. We will follow the traditional way to introduce DFT as sketched in these references. For a discussion of DFT based on an alternative, thermodynamical approach, we refer to [132].
5.2 The electron density.

Let us now focus on the observable that plays a crucial role in Density Functional Theory: the one-body electron density. Conventional many-body approaches describe a system with \( N \) electrons at positions \( x_1, x_2, \ldots, x_N \) (where \( x \) comprises the spatial variable \( \mathbf{r} \) and the spin degree of freedom \( \sigma \)) by means of the \( N \)-particle wave function \( \Psi(x_1, x_2, \ldots, x_N) \) (properly antisymmetrized and normalized to unity). The probability density to find the electrons at coordinates \( x_1, x_2, \ldots, x_N \) is

\[
\rho_N(x_1, x_2, \ldots, x_N) = |\Psi(x_1, x_2, \ldots, x_N)|^2, \tag{5.1}
\]

where we have introduced the \( N \)-particle probability density \( \rho_N(x_1, x_2, \ldots, x_N) \). The one-particle density is then defined as:

\[
\rho(\mathbf{r}) = N \sum_\sigma \int dx_2 \ldots \int dx_N \rho_N(x_1, x_2, \ldots, x_N), \tag{5.2}
\]

which is interpreted as the probability to find one electron at coordinate \( \mathbf{r}_1 \), while the other \( N-1 \) electrons have arbitrary positions and spin in the state represented by \( \Psi \). More generally, we can also introduce the one-body density matrix (where the coordinates \( \mathbf{r}_1 \) and \( \mathbf{r}'_1 \) act as continuous “indices” for the quantity \( \rho_1 \))

\[
\rho_1(\mathbf{r}_1, \mathbf{r}'_1) = N \sum_\sigma \int dx_2 \ldots \int dx_N \Psi(\mathbf{r}_1, x_2, \ldots, x_N) \Psi^*(\mathbf{r}'_1, x_2, \ldots, x_N). \tag{5.3}
\]

It is clear that the one-particle density is the diagonal of this matrix (\( \mathbf{r}_1 = \mathbf{r}'_1 \)):

\[
\rho(\mathbf{r}) = \rho_1(\mathbf{r}, \mathbf{r}) = \rho_1(\mathbf{r}, \mathbf{r}').
\]

In the case of systems in which the external potential is generated by pointlike positive charges, we can intuitively understand why the electron density can serve as the main quantity from which all other observables can be calculated. First, due to the normalization of the many-body wave function it contains the number of electrons present in the system \( \int d^3r \rho(\mathbf{r}) = N \). Next, in the region very close to an atom in the molecule or solid, the electron density exhibits a maximum with a finite value. The gradient of the density shows a discontinuity at this position, which is the so-called cusp. This cusp is caused by the singularity of the potential generated by the atomic nucleus in the hamiltonian. In fact, it can be shown that the cusp is related to the nuclear charge \( Z_A \) of nucleus \( A \) \cite{134}

\[
\lim_{\mathbf{r} \to \mathbf{r}_A} \left[ \frac{\partial}{\partial r} + 2 Z_A \right] \rho(\mathbf{r}) = 0, \tag{5.4}
\]

where \( \overline{\rho}(\mathbf{r}) \) is the spherical average of \( \rho(\mathbf{r}) \) around \( \mathbf{r}_A \). This means that the density determines the nuclear charges, which implies that the total hamiltonian is known from the density, provided that the two-body interaction is specified. Furthermore,
we also note that the asymptotic behavior of the density at infinity determines the first ionization energy $I$ of the system. In fact, for finite systems with a nondegenerate $N$-electron ground state, the asymptotic behavior of the density is \[ \rho(r) \to r^{2\nu} e^{-2\kappa r} \] in which $\kappa = \sqrt{2I}$, $r = |r|$, and $\nu = \frac{Z_N - N + 1}{\kappa} - 1$ (where $Z_N$ is the total charge of all nuclei).

On behalf of completeness, we note that the electron density can be determined experimentally by using X-ray diffraction.

Furthermore, we can introduce another integrated form of the $N$-particle density, the pair density

\[ \rho_2(\vec{r}_1, \vec{r}_2) = \frac{N(N-1)}{2} \sum_{\sigma_1} \sum_{\sigma_2} \int dx_3 \ldots \int dx_N \rho_N(x_1, x_2, \ldots, x_N). \]  \hspace{1cm} (5.5)

This quantity is also referred to as the diagonal two-body density matrix and can be used to cast some expressions in a more elegant form. It represents the probability to find a pair of electrons in a volume element $d^3r_1$ around $\vec{r}_1$ and $d^3r_2$ around $\vec{r}_2$. The pair density is very useful in the representation of exchange and correlation effects. More specifically, it can be used in the expression for the electron-electron interaction as follows:

\[ E_{ee} = \langle \Psi | \frac{1}{2} \sum_{i,j=1}^N \frac{1}{r_{ij}} | \Psi \rangle = \int d^3r_1 \int d^3r_2 \frac{\rho_2(\vec{r}_1, \vec{r}_2)}{r_{12}}, \]  \hspace{1cm} (5.6)

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$. The pair density is symmetric with respect to an interchange of the coordinates of the particles and is normalized in this work to the total number of distinct pairs, following [130] and [135]. Other normalizations also exist, e.g. to the number of nondistinct pairs such as in [136]. Of course, the discussion of the density (matrix) can be extended to cover spin densities: we only have to add the spin polarization, while also the summation over the spin is to be discarded in the definitions (5.2) and (5.5).

Eq. (5.6) can be split into two contributions by introducing the exchange-correlation hole $h_{xc}(\vec{r}_1; \vec{r}_2)$:

\[ \rho_2(\vec{r}_1, \vec{r}_2) = \frac{\rho(\vec{r}_1)}{2} [\rho(\vec{r}_2) + h_{xc}(\vec{r}_1; \vec{r}_2)]. \]  \hspace{1cm} (5.7)

The ratio $f(\vec{r}_1; \vec{r}_2) = h_{xc}(\vec{r}_1; \vec{r}_2)/\rho(\vec{r}_2)$ is sometimes called the correlation factor or the pair correlation function [130]. The exchange-correlation (xc) hole is related to the conditional amplitude $\Omega(\vec{r}_2; \vec{r}_1) = \frac{2\rho(\vec{r}_1, \vec{r}_2)}{\rho(\vec{r}_1)}$ [where the additional factor 2 arises due to the normalization in Eq. (5.5)]:

\[ h_{xc}(\vec{r}_1; \vec{r}_2) = \Omega(\vec{r}_2; \vec{r}_1) - \rho(\vec{r}_2). \]  \hspace{1cm} (5.8)
The conditional amplitude represents the probability to find any electron at position \( \vec{r}_2 \) provided that we know that there is already one electron at \( \vec{r}_1 \). Expression (5.8) shows that the xc hole accounts for all effects that correlate the electron positions, i.e. exchange and other electron-electron effects: if there is no correlation at all, the conditional amplitude \( \Omega(\vec{r}_2; \vec{r}_1) \) reduces to \( \rho(\vec{r}_2) \) and the hole is identical to zero. Note, however, that this reasoning leads to an incorrect normalization of the pair density; more correctly \( \Omega(\vec{r}_2; \vec{r}_1) \) reduces to \( \frac{N-1}{N}\rho(\vec{r}_2) \) in the absence of correlations. Correlation typically leads to a depletion of the electron density \( \rho \) at \( \vec{r}_2 \) as compared to the independent-particle case, which causes the xc hole to be negative, especially near the reference electron at \( \vec{r}_1 \) (hence the name of the xc hole). Since the conditional amplitude integrates to \( N-1 \), we find that the xc hole contains the charge of exactly one electron:

\[
\int d^3r_2 \ h_{xc}(\vec{r}_1; \vec{r}_2) = -1.
\] (5.9)

This important equation is referred to as the sum rule for the xc hole and supports the idea that the reference electron at position \( \vec{r}_1 \) actually “digs” a hole in the total electron pair density. The xc hole diminishes the probability to find an electron nearby another one due to the correlations. Note that Eq. (5.9) is independent of the reference position \( \vec{r}_1 \).

Using the xc hole, Eq. (5.6) can be written in a more explicit form:

\[
E_{ee} = \frac{1}{2} \int d^3r_1 \int d^3r_2 \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{r_{12}} + \frac{1}{2} \int d^3r_1 \int d^3r_2 \frac{\rho(\vec{r}_1) h_{xc}(\vec{r}_1; \vec{r}_2)}{r_{12}}.
\] (5.10)

We clearly recognize the classical Coulomb repulsion between two charge distributions in the first term. This term is also called the Hartree term. The second term, on the other hand, accounts for all quantum-mechanical aspects described by the interaction of the charge density \( \rho \) with the charge distribution of the xc hole \( h_{xc} \). A very important correction that should be included in the second term is the so-called self-interaction correction. Self-interaction implies that an electron interacts with itself, contrary to the pointlike nature of the particle. Not all computational schemes are free from self-interaction. The Hartree-Fock scheme is an example of a method that is self-interaction free. We can see this by considering e.g. Eq. (4.3) for a hydrogenlike ion, where there is clearly no two-body interaction present. In this case, the Fock term exactly cancels the Hartree term. In DFT, it depends on the xc functional that is used whether self-interaction is present, but mostly it is. We can understand this from Eq. (5.10): the xc hole is not known exactly and therefore practical DFT calculations have to start from an approximative form. Of course, the Hartree term in Eq. (5.10) is then not necessarily cancelled by the chosen form for the hole in the DFT case. As will be discussed in section 5.5, the choice of the expression for the xc hole largely influences the accuracy of the DFT prediction and in
particular determines whether the calculation includes the spurious self-interaction.

Because the xc hole is very important in the theoretical framework of DFT, we devote a more elaborate discussion to it. Therefore, we will adopt the spin degree of freedom explicitly in the notation and introduce the spin-dependent xc hole $h_x^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2)$. It is defined as in Eq. (5.7), where the spin indices $\sigma_1$ and $\sigma_2$ are added at the appropriate positions. The spin-dependent pair density $\rho_x^{\sigma_1 \sigma_1}(\vec{r}_1; \vec{r}_2)$ is related to the total pair density $\rho_2(\vec{r}_1; \vec{r}_2)$ by

$$\rho_2(\vec{r}_1; \vec{r}_2) = \rho_2^{\uparrow \uparrow}(\vec{r}_1; \vec{r}_2) + \rho_2^{\downarrow \uparrow}(\vec{r}_1; \vec{r}_2) + \rho_2^{\uparrow \downarrow}(\vec{r}_1; \vec{r}_2) + \rho_2^{\downarrow \downarrow}(\vec{r}_1; \vec{r}_2).$$  \hspace{1cm} (5.11)

Here we have, for instance, that the spin-dependent pair density $\rho_2^{\uparrow \downarrow}(\vec{r}_1; \vec{r}_2)$ gives the probability of finding an electron with spin down at point $\vec{r}_1$ and another one with spin up simultaneously at point $\vec{r}_2$. Of course, in a likewise manner, the spin-dependent one-body density $\rho_\sigma(\vec{r})$ can be introduced: $\rho(\vec{r}) = \rho_\uparrow(\vec{r}) + \rho_\downarrow(\vec{r})$.

The spin-dependent hole can be split in a Fermi hole

$$h_x^{\sigma_1 \sigma_1}(\vec{r}_1; \vec{r}_2) = \delta_{\sigma_1 \sigma_2} h_x^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2)$$  \hspace{1cm} (5.12)

and a Coulomb hole $h_c^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2)$:

$$h_x^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2) = h_x^{\sigma_1 \sigma_1}(\vec{r}_1; \vec{r}_2) + h_c^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2).$$  \hspace{1cm} (5.13)

As reported in Ref. [137], there are numerous definitions available for the Fermi hole ([138]-[140]) and several for the Coulomb hole ([141]-[143]). Here, we will follow Gopinathan et al. [138], who define the Fermi hole as

$$\rho_2^{\sigma_1 \sigma_1}(\vec{r}_1; \vec{r}_2) = \frac{\rho_\sigma(\vec{r}_1)}{2} - \rho_x^{\sigma_1 \sigma_1}(\vec{r}_1; \vec{r}_2),$$  \hspace{1cm} (5.14)

Note that we added a factor $1/2$ in this definition compared with Gopinathan et al., because these authors normalize the pair density to the number of nondistinct pairs. From the definition of the Fermi hole in Eq. (5.14), the Coulomb hole is specified as well, by means of Eqs. (5.13) and (5.7).

The Fermi or exchange hole includes the exchange effects due to the Pauli principle and only applies to electrons with the same spin projection. It represents the type of quantum-mechanical influence that has been accounted for in the Hartree-Fock approach and dominates by far the Coulomb hole (this is why Hartree-Fock is already a good approximative description of a many-electron system). The sum rule for the exchange hole is very similar to the one of the total hole [Eq. (5.9)]

$$\int d^3 r_2 h_x^{\sigma_1 \sigma_1}(\vec{r}_1; \vec{r}_2) = -1,$$  \hspace{1cm} (5.15)

and means that the exchange hole removes one electron of the same spin as the reference electron from the total electron density: this sum rule ensures that self-interaction is corrected for. Furthermore, we know that two electrons with the same
spin cannot occupy the same point in space, and therefore we obtain the following limit (where \( \vec{r}_1 \) is the position vector of the reference electron)
\[
\lim_{\vec{r}_2 \to \vec{r}_1} h_x^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2) = -\rho_{\sigma_1}(\vec{r}_1).
\]
(5.16)

Also, it can be shown that
\[
h_x^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2) \to -\frac{\rho_{\sigma_1}(\vec{r}_2)}{N_{\sigma_1}} \quad \text{if} \quad |\vec{r}_1 - \vec{r}_2| \to \infty,
\]
(5.17)
where \( N_{\sigma_1} \) is the number of electrons with spin \( \sigma_1 \). Furthermore, we have that \( h_x^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2) \leq 0 \) everywhere.

On the other hand, the Coulomb hole incorporates correlations in the motion of the electrons due to the Coulomb interaction and is independent of the relative spin polarization of the two electrons. By definition, correlations are the residual two-body interactions that are not taken into account in the Hartree-Fock technique. The sum rule for the Coulomb hole is
\[
\int d^3 r_2 \ h_x^{\sigma_1 \sigma_2}(\vec{r}_1; \vec{r}_2) = 0.
\]
(5.18)

This means that, unlike the Fermi hole, the Coulomb hole will not have a fixed sign. Because the correlation hole is caused by the electrostatic repulsion of the electrons, we expect the correlation hole to be negative close to the reference electron (which pushes the other electrons away). However, to obey sum rule (5.18), the Coulomb hole must be positive in the region farther away from the reference electron. Negative and positive contributions to the correlation hole cancel each other to satisfy sum rule (5.18).

We end this section with two notes. First, we remark that it is clear that the hole functions mentioned here do not have any relation with the particle and hole spectral functions introduced in chapter 2 [see Eqs. (2.20) and (2.21)]. Second, we stress that the separation into Fermi and Coulomb hole is in fact artificial: only the total \( xc \) hole has a real physical significance. Yet, in section 5.5.2 it will become clear that, in the search for approximative functionals, the splitting in exchange and correlation is used quite often. In this respect, we note that, although it was mentioned above that various definitions for this splitting exist, a majority of the DFT community now follows the separation introduced by C. Filippi, C.J. Umrigar, and X. Gonze [144]. Their separation is used in chapter 6, where we will also study exchange and correlation energies [see Eq. (6.22)].

5.3 The Hohenberg-Kohn theorems.

We will now show that the density-functional formalism is equally sound as wavefunction based theories like the standard Hartree-Fock method. As indicated in the
introduction, only an integrated quantity like the electron density remains manageable when studying intricate systems with a large number of particles. In this section, the founding theorems (due to Hohenberg and Kohn [145]) of DFT are discussed for local, spin-independent external potentials that lead to a nondegenerate ground state. These theorems have been discussed extensively in the literature: besides the original paper by Hohenberg and Kohn [145] and the review works on DFT that were mentioned before, we also refer to [146] and [147]. We note in particular that in the former reference, a rigorous foundation of density functional theory is given.

The first theorem of Hohenberg and Kohn states that no information is lost when choosing the ground-state electron density $\rho_\alpha(\vec{r}_1)$ instead of the ground-state $N$-body wave function $\Psi_\alpha(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ as the central object in the theory. Moreover, it also proves that for a system of electrons interacting via the Coulomb force, the electron density and the external potential $v(\vec{r}_1)$ acting on the particles are in a one-to-one relationship as well. In short, we assume that we know how many particles are present in the system (normalization of the electron density) and what is the two-body interaction between the particles. In this way, the external potential is the only degree of freedom in the Hamiltonian. The first theorem of Hohenberg and Kohn then states that

$$v(\vec{r}_1) \Leftrightarrow \Psi_\alpha(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \Leftrightarrow \rho_\alpha(\vec{r}_1).$$

From a puristic point of view, we note that the Hohenberg-Kohn theorem only considers densities and wave functions that can a priori be derived from a one-body potential, i.e. Hohenberg and Kohn assumed that there is at least one potential that corresponds to a given single-particle density or $N$-particle wave function and then proved that there is only one such potential. To stress this, we add an index $\nu$ to the density and wave function. The discussion of this assumption will be continued after the proof of the theorems.

Some of the relations of Eq. (5.19) are derived easily in one sense (the other sense is less obvious). Let us consider a system of $N$ electrons with the Coulomb force as two-body interaction $W$, described by the Hamiltonian $\hat{H} = T + V + W$. With this form for the Hamiltonian, we can define a class of Hamiltonians by introducing a set of local one-body potentials $V$. Each element of this set leads to a ground state for the system of $N$ fermions by means of the Schrödinger equation

$$\hat{H} | \Psi_\nu \rangle = E_{2\nu} | \Psi_\nu \rangle,$$

where $E_{2\nu}$ is the ground-state energy of the system and $| \Psi_\nu \rangle$ is the corresponding $N$-particle wave function. We restrict the discussion here to nondegenerate ground states. Extensions of the formalism to cover degenerate systems are possible by means of ensemble theory [148]. We can group the $N$-particle ground-state wave
functions in a set $\Psi$. It is evident that the Schrödinger equation provides a relation with $\mathcal{V}$, the map

$$A : \mathcal{V} \Rightarrow \Psi,$$

(5.21)

is surjective: each element of $\Psi$ is associated with some element of $\mathcal{V}$. As mentioned before, this is actually the premise from which Hohenberg and Kohn started the proof.

Let us now consider the relation between the $N$-particle wave function and the single-particle (s.p.) density. It is well-known that we can calculate the ground-state density $\rho(\vec{r})$ from the $N$-particle ground-state wave function $|\Psi\rangle$ [see also Eq. (2.25)]

$$\begin{align*}
\rho(\vec{r}) &= \langle \Psi | \hat{\rho}(\vec{r}) | \Psi \rangle = \langle \Psi | \sum_{\sigma} c^\dagger(\vec{r}\sigma)c(\vec{r}\sigma) | \Psi \rangle \\
&= N \sum_{\sigma} \int dx_2 \ldots \int dx_N | \Psi(\vec{r}\sigma,x_2,\ldots,x_N) |^2.
\end{align*}$$

(5.22)

In this expression, $c^\dagger(\vec{r}\sigma)$ [$c(\vec{r}\sigma)$] is a creation (annihilation) operator of a particle at coordinate $(\vec{r},\sigma)$. We now define the set $\mathcal{N}$ which groups all possible densities that can be derived from the elements in $\Psi$. Based on Eq. (5.22) we can establish a second map:

$$B : \Psi \Rightarrow \mathcal{N},$$

(5.23)

which is clearly a surjective relation as well.

The value of the first Hohenberg-Kohn theorem is to prove that the relations $A$ and $B$ are bijective and therefore invertible [Eq. (5.19)]. We will now proceed to the proof of the first theorem of Hohenberg-Kohn, which uses the technique of *reductio ad absurdum*.

First the unique relationship between the one-body potential and the wave function will be proven: $\mathcal{V} \Leftrightarrow \Psi$. From the discussion above, we know that only the fact that the external potential is determined uniquely by the $N$-body wave function is nontrivial and therefore we will focus on proving that knowledge of the $N$-particle wave function unambiguously determines the potential: $v(\vec{r}_1) \Leftrightarrow \Psi_\nu(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$.

Suppose that two spin-independent one-body potential operators $\hat{V}$ and $\hat{V}'$ give rise to the same $N$-particle wave function $|\Psi_\nu\rangle = |\Psi_\nu'\rangle$, which describes a nondegenerate ground state. The potential operators $\hat{V}$ and $\hat{V}'$ are supposed to differ in a nonevident way, i.e. in coordinate space they differ in more than just an additive constant. We then have two distinct Schrödinger equations:

$$\begin{align*}
\hat{H} |\Psi_\nu\rangle &= (\hat{T} + \hat{V} + \hat{W}) |\Psi_\nu\rangle = E_{gs} |\Psi_\nu\rangle, \\
\hat{H}' |\Psi_\nu\rangle &= (\hat{T} + \hat{V}' + \hat{W}) |\Psi_\nu\rangle = E'_{gs} |\Psi_\nu\rangle.
\end{align*}$$

(5.24)

By subtracting both equations, we obtain

$$\langle \hat{V} - \hat{V}' |\Psi_\nu\rangle = (E_{gs} - E'_{gs}) |\Psi_\nu\rangle,$$

(5.25)
In coordinate space, we have that

\[ [v(\vec{r}_1) - v'(\vec{r}_1)] \Psi_v(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \lambda \Psi_v(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N). \]  

(5.26)

Because \( \nabla \) and \( \nabla' \) are multiplicative operators, we can now eliminate the wave function in Eq. (5.26) if \( \Psi_v(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \neq 0 \). Since the wave function will only vanish in isolated points (provided the potential corresponding to \( | \Psi_v \rangle \) is well-behaved), we conclude, due to the fact that \( v(\vec{r}_1) - v'(\vec{r}_1) \) should be continuous, that in every point in space \( v(\vec{r}_1) - v'(\vec{r}_1) \) equals a constant, in contradiction with the premise. This concludes the proof of the invertibility of map \( A \) [Eq. (5.21)] for spin-independent potentials which differ in more than a trivial constant, in the case of nondegenerate ground states.

We will now prove that the ground-state electron density and the \( N \)-particle ground-state wave function involve the same information: \( \rho_e(\vec{r}_1) \leftrightarrow \Psi_v(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \). If we only focus on the nontrivial part of this statement, it means that a given one-body density can only be generated by one unique wave function in \( \Psi \) (up to some arbitrary phase factor). Let us assume that two distinct \( N \)-particle ground-state wave functions \( \Psi_v(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \) and \( \Psi'_v(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \) lead to the same \( \rho_e(\vec{r}_1) \). From the proof of the first part we know that the hamiltonians corresponding to the two wave functions are different.

Due to the Rayleigh-Ritz variational principle for arbitrary \( N \)-particle wave functions \( | \Psi \rangle \)

\[ E_{gs} = \min_{\Psi} \left[ \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \right], \]

we obtain in case of the nondegenerate ground state \( | \Psi_v \rangle \)

\[ E_{gs} = \langle \Psi_v | \hat{H} | \Psi_v \rangle < \langle \Psi'_v | \hat{H} | \Psi'_v \rangle = \langle \Psi'_v | \hat{H}' | \Psi'_v \rangle + \langle \Psi'_v | \nabla - \nabla' | \Psi'_v \rangle = E'_{gs} + \int d^3r \rho_e(\vec{r})[v(\vec{r}) - v'(\vec{r})]. \]

(5.28)

However, if we start from hamiltonian \( \hat{H}' \), we can deduce along the same lines of reasoning that

\[ E'_{gs} < E_{gs} + \int d^3r \rho_e(\vec{r})[v'(\vec{r}) - v(\vec{r})]. \]

(5.29)

Note that we have used here that the two wave functions lead to the same density \( \rho_e(\vec{r}) \). It is clear that Eqs. (5.28) and (5.29) exclude each other due to the strict inequality, which concludes the proof.

The bijective relation between the ground-state \( N \)-particle wave function and the ground-state electron density implies that all observables become a functional of the density. For an arbitrary operator \( \hat{O} \) we obtain:

\[ O[\rho_e] = \langle \Psi[\rho_e] | \hat{O} | \Psi[\rho_e] \rangle, \]

(5.30)
where $| \Psi[\rho_e] \rangle$ is that wave function which minimizes the hamiltonian and corresponds to the density $\rho_e$. This equation justifies the choice of the electron density as a central variable in the formalism. We denote a functional by square brackets (see App. D), as opposed to a function, which is characterized by round brackets. In particular, the total energy becomes a functional in the density:

$$E[\rho_e] = \langle \Psi[\rho_e] \mid \hat{T} + \hat{W} + \hat{V} \mid \Psi[\rho_e] \rangle.$$  \hfill (5.31)

From the Rayleigh-Ritz variational principle we derive that the functional $E[\rho]$ has the property:

$$E[\rho^0_e] < E[\rho_e] \quad \text{for} \quad \rho_e \neq \rho^0_e,$$  \hfill (5.32)

where $\rho^0_e$ is the (nondegenerate) ground-state density which corresponds to the ground-state energy

$$E_{gs} = E[\rho^0_e] = \min_{\rho_e \in \mathcal{N}} E[\rho_e].$$  \hfill (5.33)

As mentioned above, the one-body potential $\hat{V}$ is the only degree of freedom left in the hamiltonian within the Hohenberg-Kohn theory. It is therefore interesting to divide the hamiltonian in a part that involves the external potential and one that is universal for all Coulomb systems that we study:

$$E[\rho_e] = \langle \Psi[\rho_e] \mid \hat{T} + \hat{W} \mid \Psi[\rho_e] \rangle + \int d^3r \, v(\vec{r}) \rho_e(\vec{r})$$

$$= F_{HK}[\rho_e] + \int d^3r \, v(\vec{r}) \rho_e(\vec{r}).$$  \hfill (5.34)

The functional $F_{HK}[\rho_e]$ has the same form in terms of the density for atoms, molecules, and solids since in each case the two-body interaction $\hat{W}$ is the Coulomb repulsion. Any external influence (respectively from one nucleus, several nuclei, or the crystal lattice) is comprised within the second term of Eq. (5.34). We note that the explicit form of $F_{HK}[\rho_e]$ in terms of the density is not known and therefore approximations must be developed before the scheme can be started. Examples of such approximations will be given in section 5.5.

The concepts of invertibility [Eq. (5.19)], variational basis [Eq. (5.32)], and universality ($F_{HK}[\rho_e]$) are the three cornerstones of the Hohenberg-Kohn theory. Also note that the theorems are only valid for ground-state properties. We do not cover the extension to excited states in this work. Statement (5.32) is known as the second theorem of Hohenberg and Kohn. It provides us with an equation to determine the ground-state density in a direct way, without having to resort to the ground-state wave function. We have to minimize the energy functional (5.34) with respect to the density $\rho_e(\vec{r})$ under the restriction that $\int d^3r \, \rho_e(\vec{r}) = N$, where $N$ is the number of particles in the system (assumed fixed in the theorems of Hohenberg-Kohn). From the Lagrange theory on variational calculus (see App. D), we obtain that the
The following equation should be satisfied for arbitrary variations of the ground-state density:

$$\delta \{ E[\rho_v] - \mu \int d^3r \; \rho_v(\vec{r}) - N \} = 0,$$

where $\mu$ is a Lagrangian multiplier. This multiplier ensures that the minimization of Eq. (5.35) leads to a density normalized to the correct number of particles. We then derive the Euler-Lagrange equation

$$\frac{\delta E[\rho_v]}{\delta \rho_v(\vec{r})} = \frac{\delta F_{HK}[\rho_v]}{\delta \rho_v(\vec{r})} + v(\vec{r}) = \mu.$$ 

The solution $\rho_v(\vec{r})$ depends on the parameter $\mu = \mu(N)$, which is determined such that the boundary condition $\int d^3r \; \rho_v(\vec{r}) = N$ is satisfied. Note that the Hohenberg-Kohn theory can be extended to systems with a fractional number of electrons by normalizing the density to a fractional number. In this extended framework it can be shown that $\mu(N)$ is the chemical potential of the system we are trying to calculate, i.e. $\mu(N) = \frac{\partial E}{\partial N}$. To illustrate this, let us consider the difference of the ground-state energies of the system with $N + \eta$ particles (where $\eta$ is infinitesimally small) and one with $N$ particles

$$E_{N+\eta} - E_N = \int d^3r \; \frac{\delta E[\rho_v^N]}{\delta \rho_v^N} \mid_{\rho_v^N} \left[ \rho_v^{N+\eta}(\vec{r}) - \rho_v^N(\vec{r}) \right]$$

$$= \int d^3r \; \mu(N) \left[ \rho_v^{N+\eta}(\vec{r}) - \rho_v^N(\vec{r}) \right]$$

$$= \mu(N) \eta,$$

which was to be demonstrated, if the limit $\eta \to 0$ is taken. A very peculiar property of the chemical potential, defined through the exact Hohenberg-Kohn energy functional in Eq. (5.36), is that it is not a continuous function of the number of particles. Indeed, as was first argued by Perdew et al. in [149], if $\mu(N)$ were continuous there would be a net electron transfer between two neutral atoms with a different chemical potential, even if they were so far away that no interaction between the two atoms is possible. This transfer would lower the total energy by creating a net charge on the atoms, which is clearly unphysical if the atoms are well separated.

The discontinuity of the chemical potential is transferred by the Euler-Lagrange equation (5.36) into a derivative discontinuity of the total-energy functional. The ideas proposed by Perdew et al. will be further elaborated upon in section 5.5.5 and in chapter 6.

The Euler-Lagrange equations provide a theoretical means to find the ground-state density, but are practically not very useful if we do not know how to construct the universal functional $F_{HK}[\rho_v]$ explicitly. It is clear that we will only find the
correct ground-state density if the form of $F_{HK}[\rho]$ is known exactly. However, the Hohenberg-Kohn theorems only set the stage and do not provide clues on how to derive this quantity. Given the complexity of many-electron problems, it is expected that the explicit construction of the universal functional is only possible for approximate systems, which will hopefully be adequate. Furthermore, suppose that we are interested in the $N$-body wave function, there is no obvious way to perform the inversion process from ground-state density to the ground-state wave function. Formally, we can solve this problem if we restate the second theorem of Hohenberg-Kohn [Eq. (5.32)] by performing the minimization procedure in two steps:

$$
E_{gs} = \min_{\Psi} \langle \Psi | \hat{T} + \hat{W} + \hat{V} | \Psi \rangle
\quad = \min_{\rho} \{ \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W} + \hat{V} | \Psi \rangle \}
\quad = \min_{\rho} \{ \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle + \int d^{3}r \, v(\vec{r})\rho(\vec{r}) \}. 
$$

(5.38)

This step-by-step procedure of minimizing the energy is called the Levy-Lieb constrained search (see [146], [150], and [153]). Here, we first fix the density and try to find the minimum energy over all wave functions that lead to that density. The resulting expression is then minimized over the electron densities to arrive at the ground-state density. Eq. (5.38) allows us to redefine the universal functional in Eq. (5.34) as

$$
F[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle. 
$$

(5.39)

Although the Levy-Lieb method formally provides a means to select the ground-state wave function, it is not a practical method: how can we ever cover all wave functions that correspond to a given density and subsequently determine which one minimizes the energy? Fortunately, there is, however, no need for a wave function in DFT: all observables can be calculated from the s.p. density directly, by virtue of the first Hohenberg-Kohn theorem.

The Levy-Lieb constrained search also solves another formal problem that is more subtle in nature. In the discussion of the Hohenberg-Kohn theorems, we have introduced a class of hamiltonians which is generated by the class of one-body potentials $\mathcal{V}$. It is clear that in the variational search of Eq. (5.32) and in the Euler-Lagrange equation (5.36), we consider only electron densities that correspond to a potential from $\mathcal{V}$. Such densities are called $\nu$-representable. However, an arbitrary electron density may of course be non-$\nu$-representable. Unfortunately, the conditions for $\nu$-representability are not known to the present day. In this respect, we mention the study of this problematic issue by Van Neck et al. [151] for one-body density matrices $\rho(\vec{r}_{1}, \vec{r}_{2})$ in case of a few simple systems. The reformulation (5.38) of the variational principle in DFT by Levy and Lieb extends the range of densities in the minimization procedure to densities that are only associated with an antisymmetrized $N$-particle wave function, without an explicit connection to the external
potential. Therefore, we also discarded the index \( v \) in Eq. (5.38). This kind of densities is referred to as the class of the \( N \)-representable densities. Furthermore, the requirements for \( N \)-representability are well-known [152]

\[
\rho(\hat{r}) \geq 0, \quad \int d^3 r \rho(\hat{r}) = N, \quad \text{and} \quad \int d^3 r \left| \nabla \rho(\hat{r}) \right|^2 < \infty. \tag{5.40}
\]

A review of the general \( N \)-representability problem of density matrices can be found in [147]. For explicit examples of reasonably well-behaved and nonnegative functions that are non-\( v \)-representable, the reader is referred to [146], [153], and [154].

One final note on the founding theorems concerns the proof of the first Hohenberg-Kohn theorem for spin-dependent problems. In this case, the reasoning leading to the invertibility of map \( \mathcal{A} (\mathcal{V} \to \Psi) \) can no longer be extended (note that in this case the set \( \mathcal{V} \) must be enlarged to cover external magnetic fields as well): in spin-dependent DFT, the map \( \mathcal{A} \) remains purely surjective (see e.g. [103]). However, the second part of the first Hohenberg-Kohn theorem, which relates the \( N \)-particle wave function uniquely to the (spin-)density and \textit{vice versa} (\( \Psi \leftrightarrow \mathcal{N} \)), remains intact also in the spin-dependent case. This is sufficient to establish a Hohenberg-Kohn-like variational principle. Also, the relations connecting the ingredients of the basic theorem are sometimes stated otherwise: the map \( \mathcal{N} \leftrightarrow \mathcal{V} \) is a universal one-to-one relation and can therefore be used as founding theorem for Density Functional Theory (instead of the map \( \Psi \leftrightarrow \mathcal{N} \)). The complementary map \( \mathcal{V} \to \Psi \) is always surjective but becomes invertible only in the case of conventional DFT which describes a spin-independent and nondegenerate ground state (see e.g. Vignale [155] for a more elaborate discussion of the spin-dependent case).

The Hohenberg-Kohn theory has enjoyed some success as a practical density functional theory, because the numerical effort to solve Eq. (5.36) is essentially independent of the number of particles in the system. Approximate functionals that can be used in the Hohenberg-Kohn formalism will be discussed in section 5.5. However, some deficiencies appear that are not easily overcome within the Hohenberg-Kohn scheme: the functionals that can be implemented in a manageable scheme show difficulties in describing the asymptotic regions of the density (close to the nuclei and at infinity), and, more importantly, fail to reproduce the shell structure in the radial density \( \left| r^2 \rho (r) \right| \). Moreover, the theory incorrectly predicts the nonexistence of negative ions and diatomic molecules (at least with the simplest functionals, see section 5.5). Therefore, present-day DFT calculations prefer a self-consistent approach, in which the electron density of the interacting system is constructed by means of s.p. orbitals of a noninteracting system, similar to the Hartree-Fock method. This practical way to perform DFT calculations will be discussed in the next section.
5.4 The Kohn-Sham scheme.

5.4.1 Introduction.

To alleviate the problems encountered in pure Hohenberg-Kohn theory, we can use a scheme proposed by Kohn and Sham [156]. It introduces s.p. orbitals in DFT, in a manner similar to Hartree-Fock but without making approximations concerning the physical, interacting many-body system. This scheme is by far the most practical way of studying complex many-electron systems within the density-functional formalism. The idea of Kohn and Sham was to try to calculate as much of the kinetic energy as possible in an exact way. It was mentioned in the previous section that the construction of the kinetic energy and the two-body interaction as a direct functional in the one-particle density is quite problematic. However, in a noninteracting system, the hamiltonian is simple since it consists only of one-body operators

$$\hat{H}_s = \hat{T} + \hat{V}_s,$$  \hspace{1cm} (5.41)

the kinetic energy and external potential respectively (we add an additional index to stress that the hamiltonian corresponds to a noninteracting s.p. system). The spectrum of this hamiltonian is derived using the Schrödinger equation

$$[-\frac{\nabla^2}{2} + v_s(\vec{r})] \phi_\alpha(\vec{r}) = \epsilon_\alpha \phi_\alpha(\vec{r}),$$  \hspace{1cm} (5.42)

where $\alpha$ denotes all quantum numbers required to specify the orbital. Provided that the ground state is nondegenerate, the corresponding density $\rho_s(\vec{r})$ has a unique representation in terms of the lowest $N$ orbitals (where $N$ is the number of particles in the system):

$$\rho_s(\vec{r}) = \sum_{\alpha=1}^{N} | \phi_\alpha(\vec{r}) |^2.$$  \hspace{1cm} (5.43)

The noninteracting system can be studied in a straightforward and exact way, in particular the kinetic energy can be accessed without making approximations. The universal kinetic-energy functional of noninteracting particles can be calculated by means of the s.p. orbitals $\{ \phi_\alpha(\vec{r}) \}$ as:

$$T_s[\rho_s] = \sum_{\alpha=1}^{N} \int d^3r \ \phi_\alpha^*(\vec{r})(-\frac{\nabla^2}{2})\phi_\alpha(\vec{r}),$$  \hspace{1cm} (5.44)

in which the sum runs again over the $N$ lowest-lying orbitals. In this way, $T_s[\rho_s]$ is only an implicit functional of the density $\rho_s$, via the s.p. orbitals and Eq. (5.43). Following the Hohenberg-Kohn theorem, we then have the following unique energy functional for the noninteracting system

$$E_s[\rho_s] = T_s[\rho_s] + \int d^3r \ v_s(\vec{r}) \rho_s(\vec{r}),$$  \hspace{1cm} (5.45)
Note that the variational equation
\[
\frac{\delta E_s[\rho_s]}{\delta \rho_s(\mathbf{r})} = \mu_s \tag{5.46}
\]
gives us an alternative means to find the exact ground-state density \( \rho_s(\mathbf{r}) \) corresponding to \( \hat{H}_s \). The parameter \( \mu_s \) is the chemical potential of the noninteracting system [compare with Eq. (5.36)].

With this in mind, Kohn and Sham introduced a fictitious system of noninteracting particles that is related to the interacting system under study by the condition that the one-electron density in both systems is identical: \( \rho_s(\mathbf{r}) = \rho(\mathbf{r}) \). This is a central condition which can be met by choosing the one-body potential acting on the noninteracting system such that it moulds the noninteracting density in the correct shape. This implies the assumption that the density \( \rho(\mathbf{r}) \) is not only \( v \)-representable in the interacting system (as required by the Hohenberg-Kohn theorems), but can also manifest itself in a noninteracting system (noninteracting \( v \)-representability).

We will discuss the central assertion of the Kohn-Sham (KS) scheme later on, after the derivation of the KS equations.

Eq. (5.44) gives us a means to calculate the kinetic energy of the noninteracting system in an exact way which involves the major part of the kinetic energy of the original interacting system. As we will see in the next subsection, all contributions to the hamiltonian of the interacting system that do not have a direct counterpart in the noninteracting one-body framework (i.e. part of the kinetic energy, the exchange interaction and correlation influences) are collected in one term that is to be approximated in practical calculations.

### 5.4.2 Derivation of the Kohn-Sham equations.

It is easily demonstrated that the Euler-Lagrange equation (5.46) for the density of the noninteracting system is equivalent with a set of Schrödingerlike equations for the s.p. orbitals. Prior to deriving these s.p. equations, we first rewrite the energy functional (5.34) of the interacting system to put it in a form like Eq. (5.45):

\[
E[\rho] = T_s[\rho] + \int d^3r \ v(\mathbf{r}) \rho(\mathbf{r}) + J[\rho] + E_{xc}[\rho], \tag{5.47}
\]

where

\[
J[\rho] = \frac{1}{2} \int d^3r_1 \int d^3r_2 \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{5.48}
\]

is the direct Coulomb interaction and

\[
E_{xc}[\rho] = F[\rho] - J[\rho] - T_s[\rho] = (T[\rho] - T_s[\rho]) + (W[\rho] - J[\rho]) \tag{5.49}
\]
is the exchange-correlation (xc) functional, which groups all other Coulomb influences. In this last expression, \( T[\rho] \) and \( W[\rho] \) respectively stand for the interacting kinetic-energy and two-body interaction functional. In Eq. (5.49) we have discarded the subindex “HK” of \( F_{HK}[\rho] \), because the universal functional can be defined more generally using the Levy-Lieb procedure [see Eq. (5.39)].

We must now find the density \( \rho(\mathbf{r}) \) for which the total energy is stationary with respect to small variations \( \delta \rho(\mathbf{r}) \) [which are restricted such that \( \rho(\mathbf{r}) + \delta \rho(\mathbf{r}) \) is still normalized to the correct number of particles and is both interacting and noninteracting \( \nu \)-representable]:

\[
0 = \delta E = E[\rho + \delta \rho] - E[\rho] = \delta T_s + \int d^3r \, \delta \rho(\mathbf{r}) \left[ v(\mathbf{r}) + v_J(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right].
\]  

(5.50)

Here, we have introduced the *Hartree potential* (the term derived from the direct Coulomb interaction)

\[
v_J(\mathbf{r}) = -\int d^3r' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|};
\]

(5.51)

and the *xc potential*

\[
v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})},
\]

(5.52)

which will be a central subject in the remaining study of this work.

Since \( \rho(\mathbf{r}) + \delta \rho(\mathbf{r}) \) is noninteracting \( \nu \)-representable, it is in a one-to-one relation with a one-body potential \( v_{\text{eff}}(\mathbf{r}) + \delta v_{\text{eff}}(\mathbf{r}) \) that generates a complete set of normalized s.p. orbitals \( \phi_\alpha(\mathbf{r}) + \delta \phi_\alpha(\mathbf{r}) \). The density has a *unique* representation in terms of these orbitals [Eq. (5.43)]. Therefore, we can further develop Eq. (5.50) using variations in the orbitals instead of variations in the density (we consider variations in \( \phi_\alpha \) and \( \phi_\alpha^* \) to be independent):

\[
\frac{\delta E[\rho]}{\delta \phi_\alpha(\mathbf{r})} = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \phi_\alpha^*(\mathbf{r})
\]

and

\[
\frac{\delta E[\rho]}{\delta \phi_\alpha(\mathbf{r})} = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \phi_\alpha(\mathbf{r}).
\]

(5.53)

We then find as a replacement for Eq. (5.50)

\[
\frac{\delta E[\rho]}{\delta \phi_\alpha(\mathbf{r})} \big|_{\phi_\alpha = \phi_{\alpha,0}} = \frac{\delta E[\rho]}{\delta \phi_\alpha^*(\mathbf{r})} \big|_{\phi_\alpha^* = \phi_{\alpha,0}} = 0.
\]

(5.54)

The condition of normalization of the density can be implemented as orthonormalization conditions on the s.p. wave functions by introducing appropriate Lagrangian multipliers \( \{\epsilon_\alpha\} \), *i.e.*

\[
\frac{\delta}{\delta \phi_\alpha^*(\mathbf{r})} \left[ E[\rho] - \sum_{\alpha=1}^N \epsilon_\alpha \left[ \int d^3r \, |\phi_\alpha(\mathbf{r})|^2 - 1 \right] \right] = 0.
\]

(5.55)
Of course, we have a similar equation for the hermitian-conjugated s.p. orbitals. Eq. (5.55) leads to the following Schrödinger-like equations

\[
\left[-\frac{\nabla^2}{2} + v_{\text{eff}}(\vec{r})\right] \phi^K_S(\vec{r}) = \epsilon^K_S \phi^K_S(\vec{r}),
\]

(5.56)

In these equations, we introduced the effective potential

\[ v_{\text{eff}}(\vec{r}) = v(\vec{r}) + v_{\text{H}}(\vec{r}) + v_{\text{xc}}(\vec{r}), \]

(5.57)

which comprises the external potential \( v(\vec{r}) \), the Hartree potential \( v_{\text{H}}(\vec{r}) \), and the xc potential \( v_{\text{xc}}(\vec{r}) \). The external potential is the one-body potential acting on the original interacting system, e.g. the potentials of the nuclei present in the system. These equations represent the Kohn-Sham equations, as indicated in the notation used in Eq. (5.56).

Note that in the derivation, we have not introduced any approximation yet: the Hohenberg-Kohn theory combined with the Kohn-Sham (KS) scheme is in principle an exact scheme. This is unlike Hartree-Fock theory, where the form of the many-body wave function of the interacting system is restricted to a single Slater determinant. Note that, of course, there are practical problems when applying DFT. First, we do not know the s.p. density of the interacting system, which is required in the Hartree potential in Eq. (5.57). Also, it is clear from the definition (5.52) that, in general, \( v_{\text{xc}}(\vec{r}) \) is only known as a functional of \( \rho(\vec{r}) \) (and not as an explicit function of \( \vec{r} \)). This implies that the KS equations are to be solved self-consistently, i.e. we make an initial guess for the KS orbitals (and hence the density), evaluate the density-dependent terms in the hamiltonian and solve the KS equations for an update of the KS orbitals (see scheme below). Of course, a self-consistent approach does not impose restrictions on the exactness of the scheme. There is, however, a more severe problem with the density-functional formalism: we do not know the explicit form of the xc functional \( E_{\text{xc}}[\rho] \) in terms of the density and therefore we do not know the functional derivative \( v_{\text{xc}}(\vec{r}) \) either. This entails that, when performing a KS calculation, we have to choose some appropriate form for the xc potential (various approximations exist for a variety of applications). This external input prevents DFT from being an exact scheme in practice.

Summarizing, a practical, self-consistent DFT-KS calculation runs as follows. First we decide what approximative functional for the xc energy (and consequently for the xc potential) to use. To stress the density-dependence of the potential, we will temporarily denote the xc potential as \( v_{\text{xc}}(\rho), \vec{r} \). In all, the following iterative scheme is performed (i.e. the Kohn-Sham scheme):

(i) Start from an initial guess for the wave functions \( \phi^K_s(\vec{r}) \) (e.g. hydrogenlike or Hartree-Fock wave functions).
(ii) Construct the density \( \rho(\vec{r}) = \sum_{\alpha=1}^{N} \mid \phi_{\alpha}^{KS}(\vec{r}) \mid^2 \).

(iii) Construct the effective potential (with the fixed approximative form for the xc potential) \( v_{\text{eff}}(\vec{r}) = v_0(\vec{r}) + v_{\text{xc}}(\rho(\vec{r})) \).

(iv) Update the set of s.p. orbitals \( \{\phi_{\alpha}^{KS}(\vec{r})\} \) by solving the KS equations \( -\nabla^2 + v_{\text{eff}}(\vec{r}) \) \( \phi_{\alpha}^{KS}(\vec{r}) = \varepsilon_{\alpha}^{KS} \phi_{\alpha}^{KS}(\vec{r}) \).

(v) Repeat the scheme from step (ii) until convergence in the s.p. energies and wave functions occurs.

The orbital approach of the KS scheme copes with some deficiencies of the Hohenberg-Kohn theory: the DFT-KS formalism is capable of describing the shell structure of the quantum-mechanical system and also predicts stable configurations for molecules.

The main problem of the KS system is the issue of finding an appropriate form for the xc potential. Unfortunately, the choice of the xc potential is often of the utmost importance since it can have a dramatic influence on the accuracy of the predictions made by the DFT-KS scheme. A survey of functionals that have been constructed over the years is presented in section 5.5. A large class of functionals discussed depend solely on the density and can be used in both pure Hohenberg-Kohn theory as well as in the DFT-KS scheme. These functionals are referred to as \textit{explicit} functionals. However, the introduction of s.p. orbitals in the KS scheme implies that we can also consider so-called \textit{implicit} functionals, \textit{i.e.} functionals that depend on the density only via the KS orbitals. The various proposals for xc potentials are tested quite elaborately on a variety of systems by the scientific community. This leads to a set of practical guidelines about what potential to use for which system, taking into account a trade-off between speed and accuracy (see \textit{e.g.} the Computational Chemistry Comparison and Benchmark Database [157]).

As a closing remark, let us discuss the apparent paradox introduced by the central condition in the construction of the KS scheme, namely that the density of the noninteracting system equals the one of the interacting system: \( \rho_0(\vec{r}) = \rho(\vec{r}) \). How can we ever check whether this condition is fulfilled if we are trying to calculate the interacting density by means of the KS procedure? The answer is provided by the xc potential and the self-consistent procedure of the KS scheme. The exact xc potential folds the two-body interaction in a one-body potential and therefore enables us to study a many-body system by solving s.p. equations. Due to the self-consistent approach, we can see intuitively that over the iterations, the quantum-mechanical many-body effects embodied in the effective potential will gradually be incorporated in the electron density of the KS scheme. At convergence, the (unique) effective potential is found that successfully moulds the noninteracting density in the correct shape, namely that of the interacting system. This statement only holds if we know
the exact xc potential. In practice, however, it depends on the amount of two-body correlations that are implemented in the approximative xc potential whether the density of the KS system will successfully simulate the density of the interacting system or not.

Finally, we address the question whether the orbitals of the KS system have a physical interpretation. From the derivation of the KS scheme, it is clear that the noninteracting system is just a mathematical construction in which the density is the sole link to the physical world. Any physical information embedded in the KS system should therefore be related to the density. In this way, we know that the number of particles in the interacting and noninteracting system is the same. Furthermore, the ionization energy of both systems is also the same (this follows from the asymptotic tail of the density, see also [158]). The key question is, however, whether the KS orbitals themselves have any physical interpretation. Until recently, the mainstream opinion was that the KS orbitals are just a mathematical tool for which the only connection with the real world is the fact that the squares of the s.p. orbitals add up to the interacting density. However, from a certain point of view, the (exact) KS orbitals are actually more real than the Hartree-Fock wave functions, which do not include correlations and do not result in the correct density. Therefore, more emphasis has arisen lately on the interpretation of the KS orbitals in qualitative molecular orbital schemes (see e.g. [159]-[162]). Nevertheless, we should add that in practice it is observed that the KS and Hartree-Fock orbitals are actually quite close. In this respect, we also refer the reader to [163]-[165] for a discussion of the relation between KS eigenvalues and excitation energies.

5.4.3 Ground-state observables in the interacting and the Kohn-Sham system.

Some important properties of the interacting many-body system that can be derived very easily from the KS scheme are the ionization energy and the total energy. As mentioned before (see chapter 4), the ionization energy can be obtained in two ways. We can either use the highest occupied KS eigenvalue (nonadiabatic approach) or use the difference in total energy between the positive ion and the neutral atom (adiabatic or relaxation approach). It was demonstrated that the latter approach is far better than the former within the DFT formalism (see e.g. Table 4.3). This observation can be attributed to the incorrect description of the asymptotic behavior of the exact xc potential in the approximative functionals. As will be discussed further, this may be caused by the fact that in the construction of the approximate functionals, only emphasis is put onto the region where the density is important. In the asymptotic region, where the density is small, the fit is less reliable. Also, as will be pointed out in section 5.5.5 and in chapter 6, the exact xc potential, considered in a system with a fractional number of electrons, features a discontinuous jump when the electron
number increases through an integer. This has implications on the predictions of the ionization energy as well. These reasons explain why the DFT predictions using the nonadiabatic procedure are often way off the correct value. The adiabatic method, involving the difference of the total energies of atom and ion, is much more reliable. The total energy can be calculated by means of Eq. (5.47). Using the KS equations, this expression can also be cast in a form which does not involve the second-order derivative of the kinetic energy:

\[
E[\rho] = \sum_{\alpha=1}^{N} e_{\alpha}^{KS} - \frac{1}{2} \int d^3r_1 \int d^3r_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} - \int d^3r \, v_{xc}(\mathbf{r}) \rho(\mathbf{r}) + E_{xc}[\rho],
\]

(5.58)

where \( \rho \) is the exact ground-state density. In this case, Eq. (5.58) yields the correct ground-state energy. We see that, similar to the well-known Hartree-Fock expression for the total energy, we have to take into account rearrangement terms next to the sum of the s.p. energies.

We stress that Eq. (5.58) yields the total energy of the interacting system:

\[
E[\rho] = \langle \Psi[\rho] | \hat{H} | \Psi[\rho] \rangle \\
= T[\rho] + W[\rho] + \int d^3r \, v(\mathbf{r}) \rho(\mathbf{r}) \\
= T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int d^3r \, v(\mathbf{r}) \rho(\mathbf{r})
\]

(5.59)

where \( | \Psi \rangle \) is the interacting many-body wave function in the ground state. The total energy of the noninteracting system (with ground-state many-particle wave function \( | \Phi \rangle \)), on the other hand, is, of course, just the sum of the s.p. energies

\[
E_s[\rho] = \langle \Phi[\rho] | \hat{H}_s | \Phi[\rho] \rangle \\
= \langle \Phi[\rho] | \hat{T} + \hat{V}_s | \Phi[\rho] \rangle \\
= \sum_{\alpha=1}^{N} e_{\alpha}^{KS}.
\]

(5.60)

Also, we note the following special property of the kinetic part \( T_s[\rho] = T[\rho] - T_s[\rho] \) of the xc-energy expression (5.49). A consequence of the Rayleigh-Ritz variational principle is that this kinetic contribution to \( E_{xc}[\rho] \) is always positive (\( T_s[\rho] \geq 0 \)): among all wave functions that result in a given ground state \( \rho(\mathbf{r}) \), \( | \Psi_0[\rho] \rangle \) is the one that minimizes

\[
\langle \Psi[\rho] | \hat{T} + \hat{W} | \Psi[\rho] \rangle,
\]

(5.61)

while the noninteracting ground-state wave function \( | \Phi_0[\rho] \rangle \) minimizes

\[
\langle \Phi[\rho] | \hat{T} | \Phi[\rho] \rangle
\]

(5.62)
as a last item in this discussion of the total energy, we focus on a method that tries to derive the energy of the physical, interacting system from the energy of the KS system in a continuous way. This procedure is called the adiabatic-connection method (ACM) \([166]-[167]\) and consists of introducing the coupling strength \(\lambda\) in the Hamiltonian which gradually incorporates two-body interactions in the description of the system \((0 \leq \lambda \leq 1)\)

\[
\hat{H}_\lambda = \hat{T} + \hat{V}_\lambda + \lambda \hat{W},
\]  

where the external potential is given by

\[
\hat{V}_\lambda = \sum \int d^3r \ c(\vec{r}) \nu(\vec{r}) \ c(\vec{r})
\]  

and the two-body operator by

\[
\hat{W} = \frac{1}{2} \sum_{\sigma_1 \sigma_2} \int d^3 \vec{r}_1 \int d^3 \vec{r}_2 \ c(\vec{r}_1 \sigma_1) c(\vec{r}_2 \sigma_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} c(\vec{r}_2 \sigma_2) c(\vec{r}_1 \sigma_1).
\]  

Both expressions are easily recognized as second-quantization forms of the diagonal one-body and the diagonal two-body operator respectively. The creation (annihilation) operator \(c(\vec{r} \sigma) [c(\vec{r} \sigma)]\) has already been introduced in Eq. \((5.22)\). Note that the kinetic energy operator \(\hat{T}\) is independent of \(\lambda\); it is a one-body operator and is therefore not influenced by the two-body interaction strength. Of course, changes in the \(N\)-body wave function due to the varying coupling strength will cause the kinetic energy \(T_\lambda(\rho)\) to change as well. Likewise, the one-body external potential \(\hat{V}\) should also be independent of \(\lambda\). Yet, we introduce a coupling-strength dependence in this potential to make the one-body density independent of the two-body interaction strength \(\lambda\). For each value of \(\lambda\), the one-body potential \(\hat{V}_\lambda\) is chosen such that the ground-state density of the various \(\lambda\)-dependent systems remains the same, i.e.

\[
\rho^\lambda(\vec{r}) = \langle \psi^\lambda | \sum_{\sigma} c^\dagger(\vec{r} \sigma) c(\vec{r} \sigma) | \psi^\lambda \rangle = \rho^{\lambda=1}(\vec{r}) = \rho(\vec{r}),
\]  

where \(| \psi^\lambda \rangle\) is the ground-state wave function of the system corresponding to coupling strength \(\lambda\). The corresponding ground-state energy can be found by means of \(E(\lambda) = \langle \psi^\lambda | \hat{H}_\lambda | \psi^\lambda \rangle\).

The total energy of the interacting system \(E_1 = E(\lambda = 1)\) can then be derived starting from the total energy of the KS system \(E_0 = E(\lambda = 0)\) by an integration over \(\lambda\)

\[
E_1 = E_0 + \int_0^1 \frac{dE(\lambda)}{d\lambda} d\lambda.
\]
Using the Hellmann-Feynman theorem [168], we find that the variation of the total ground-state energy with \( \lambda \) is given by

\[
\frac{dE(\lambda)}{d\lambda} = \langle \Psi^\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \Psi^\lambda \rangle = \frac{\partial}{\partial \lambda} \int d^3r \ v(\vec{r}) \rho(\vec{r}) + \frac{1}{2} \int d^3r_1 \int d^3r_2 \ \frac{1}{|\vec{r}_1 - \vec{r}_2|} \sum_{\sigma_1 \sigma_2} \langle \Psi^\lambda | c^\dagger(\vec{r}_1 \sigma_1) c^\dagger(\vec{r}_2 \sigma_2) c(\vec{r}_2 \sigma_2) c(\vec{r}_1 \sigma_1) | \Psi^\lambda \rangle.
\]

(5.69)

At this point, we note that an alternative definition of the diagonal two-body density matrix \( \rho_2(\vec{r}_1, \vec{r}_2) \) is given by [compare with Eq. (5.5)]

\[
\rho_2(\vec{r}_1, \vec{r}_2) = \frac{1}{2} \sum_{\sigma_1 \sigma_2} \langle \Psi^\lambda | c^\dagger(\vec{r}_1 \sigma_1) c^\dagger(\vec{r}_2 \sigma_2) c(\vec{r}_2 \sigma_2) c(\vec{r}_1 \sigma_1) | \Psi \rangle,
\]

(5.70)

where \( | \Psi \rangle \) is the many-particle (ground-state) wave function and the factor \( \frac{1}{2} \) indicates normalization to the number of distinct pairs. It is easily proven that this definition is equivalent to Eq. (5.5). Likewise, we can introduce the \( \lambda \)-dependent pair density

\[
\rho_2^\lambda(\vec{r}_1, \vec{r}_2) = \frac{1}{2} \sum_{\sigma_1 \sigma_2} \langle \Psi^\lambda | c^\dagger(\vec{r}_1 \sigma_1) c^\dagger(\vec{r}_2 \sigma_2) c(\vec{r}_2 \sigma_2) c(\vec{r}_1 \sigma_1) | \Psi^\lambda \rangle,
\]

(5.71)

and related to it, the \( \lambda \)-dependent xc hole [cf. Eq. (5.7) and Eq. (5.8)]

\[
h_{xc}^\lambda(\vec{r}_1; \vec{r}_2) = \frac{2\rho_2^\lambda(\vec{r}_1, \vec{r}_2)}{\rho(\vec{r}_1)} - \rho(\vec{r}_2).
\]

(5.72)

Combining Eqs. (5.68) and (5.69) we arrive at the important energy expression

\[
E_1 = \frac{1}{2} \int d^3r_1 \int d^3r_2 \ \frac{\rho_2^\lambda(\vec{r}_1, \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}
\]

\[
= \frac{1}{2} \int d^3r_1 \int d^3r_2 \ \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + \frac{1}{2} \int d^3r_1 \int d^3r_2 \ \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}
\]

\[
\frac{1}{2} \int d^3r_1 \int d^3r_2 \ \frac{\rho(\vec{r}_1) \tilde{h}_{xc}(\vec{r}_1; \vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|},
\]

(5.73)

where we have introduced the coupling-strength integrated xc hole \( \tilde{h}_{xc}(\vec{r}_1; \vec{r}_2) = \int d\lambda \ h_{xc}^\lambda(\vec{r}_1; \vec{r}_2) \) and where \( v(\vec{r}) = v_{\lambda=1}(\vec{r}) \). It obeys the same sum rule as the “pure” xc hole [Eq. (5.9)]. The ACM is often used in the derivation of xc functionals, as we will discuss later on.
To conclude this overview of the ACM, it is remarked that in the energy expression for the ground state of the interacting system of Eq. (5.73), we do not use the interacting kinetic energy \( T[\rho] \), but the kinetic energy \( T_s[\rho] \) of the noninteracting system. This is corrected for by the integration over \( \lambda \). To explain this in more detail, let us take a look at the ground-state energy of a system along the adiabatic-connection line (suppose at coupling strength \( \lambda \))

\[
E(\lambda) = T_\lambda[\rho] + \int d^3r \, v_\lambda(r)\rho(r) + \frac{\lambda}{2} \int d^3r_1 \int d^3r_2 \, \rho(r_1)\rho(r_2) \frac{\rho(r_1)h_{\lambda}^\rho(r_1;\rho(r_2))}{|r_1 - r_2|}.
\]

The last term of this energy expression is the xc energy \( E_{\text{xc}}^\rho[\rho] \) of the system at coupling strength \( \lambda \). It only involves potential-energy information originating from the two-body interaction functional \( \lambda(W^\lambda[\rho] - J[\rho]) \) and includes no kinetic-energy contribution (the kinetic energy \( T_\lambda[\rho] \) is the true kinetic energy of the system at coupling strength \( \lambda \)). In expression (5.73), however, such a kinetic-energy contribution to \( E_{\text{xc}}[\rho] \) is required to correct for the use of the noninteracting kinetic energy \( T_s[\rho] \). This correction is embedded within the coupling-constant integration of the xc hole: the integration process adds the difference \( T[\rho] - T_\lambda[\rho] \) to \( E_{\text{xc}}^\lambda_{\text{xc}}[\rho] \) to \( E_{\text{xc}}^{\lambda=1}[\rho] = W^{\lambda=1}[\rho] - J[\rho] \). In other words, we obtain an important simplification in Eq. (5.73) by using \( T_\lambda[\rho] \) instead of \( T[\rho] \), but to compensate for that, we have to perform an additional integration over the xc hole. This implies that the xc hole needs to be known for all values of the coupling strength. As will be discussed in section 5.5.4, a special class of functionals can be derived which includes various ways to perform the integration over the coupling constant.

So far, we have presented the DFT-KS theory in its most basic form. To end this survey on the theoretical background of DFT, we mention that several extensions of the DFT-KS concept exist [169]-[170]. A first extension is of course to include the spin degree of freedom, which leads to a spin-unrestricted scheme (see [171]). Furthermore, the theory can be extended to the finite-temperature domain which requires an ensemble-based approach [172]. Spin-dependent systems at finite temperatures can be discussed by combining the above arguments [173]. Also, a current- and spin-density functional theory for electronic systems in arbitrary strong magnetic fields has been described by Vignale and Rasolt [155]. The theory of ensembles can also be used to extend DFT to systems with degenerate ground states, to introduce levels with a fractional occupancy, and to deal with excited states (see [103]). Further extensions can be made to the case of nonlocal potentials [152] and a discussion of the relativistic formulation of DFT has been given by Rajagopal [169] and Dreizler [174]. There has been much work on time-dependent DFT as well [175], which is essential for problems such as optical absorption or frequency-dependent polarizabilities. Finally, DFT can also be founded on more general field-theoretical grounds by using the effective-action formalism (see [176]).
5.5 Approximations to the exchange-correlation functional.

In this section, we discuss a few ways to construct xc functionals for practical use in DFT. A first route leads to functionals that can be used in both pure Hohenberg-Kohn theory, or Hohenberg-Kohn combined with the KS scheme. It tries to generate functionals which explicitly depend on the one-body density. It is clear from Eq. (5.49) that approximations to the universal functional $F[\rho]$ also lead to approximations to the xc functional $E_{xc}[\rho]$. The exact $F[\rho]$ has the following form

$$F[\rho] = \min\langle \Psi | \hat{T} + \hat{W} | \Psi \rangle,$$

(5.75)

where

$$\min\langle \Psi | \hat{T} + \hat{W} | \Psi \rangle = T[\rho] + W[\rho]$$

$$= \frac{1}{2} \int d^3r_1 \left[ \nabla \rho_1 \cdot \nabla \rho_2 \right] \rho_1(\vec{r}_1, \vec{r}_2) \big|_{\vec{r}_1 = \vec{r}_2} + \int d^3r_1 \int d^3r_2 \frac{\rho_2(\vec{r}_1, \vec{r}_2)}{r_{12}}.$$  

(5.76)

This means that, in order to arrive at a functional in the one-body electron density $\rho(\vec{r})$, we need to find an expansion of the nondiagonal one-body matrix $\rho_1(\vec{r}_1, \vec{r}_2)$ and the diagonal two-body matrix $\rho_2(\vec{r}_1, \vec{r}_2)$ in terms of the diagonal one-particle density $\rho(\vec{r})$. A straightforward approximation for $\rho_2(\vec{r}_1, \vec{r}_2)$ seems to put $h_{xc}(\vec{r}_1; \vec{r}_2)$ in Eq. (5.7) equal to zero. In this way, the two-body matrix only comprises the electron-electron repulsion: $\rho_2(\vec{r}_1, \vec{r}_2) \approx \frac{1}{2} \rho(\vec{r}_1) \rho(\vec{r}_2)$ (we can also multiply with a factor $\frac{N-1}{N}$ to restore the correct normalization, see also Ref. [177]). Alternatively, we can use an approximation which includes the exchange interaction as well [130]

$$\rho_2(\vec{r}_1, \vec{r}_2) \approx \frac{1}{2} \left\{ \rho(\vec{r}_1) \rho(\vec{r}_2) - \left[ \rho_{11}(\vec{r}_1, \vec{r}_2) \rho_{11}(\vec{r}_2, \vec{r}_1) + \rho_{12}(\vec{r}_1, \vec{r}_2) \rho_{12}(\vec{r}_2, \vec{r}_1) \right] \right\},$$

(5.77)

where the arrows indicate the spin polarization of the two electrons at positions $\vec{r}_1$ and $\vec{r}_2$. With these approximations for $\rho_2$, we only need to find an expansion for the nondiagonal one-body matrix $\rho_1$.

To achieve this goal, a model system is considered that forms the basis from which almost all approximate xc functionals are derived: the electron gas. This is a system of interacting electrons in a uniformly distributed positive background. The total charge of the positive background is chosen such that the total system is neutral. The idea to use the electron gas in order to generate approximative functionals was already suggested in the original paper of Kohn and Sham [156]. In a first approximation, it is assumed that the electron gas is homogeneous (subsection 5.5.1). The perturbation expansion of the total-energy density for this system is reasonably well-known (see e.g. [2] or [103]), and various approximations to the xc
functional can be derived from it. Obviously, these approximative functionals can only be expected to work well for rather homogeneous systems, such as simple metals like sodium [178]. For atoms and molecules, however, the strong gradients present in the density near the nucleus (nuclei) can cause the homogeneous-electron-gas approximation to fail completely.

To cope with this problem, the expansion of the density matrices in Eq. (5.76) is extended to include gradients in the one-body density. Also, parameters can be added to the functional form to ensure that certain theoretical conditions on the xc potential are satisfied and to further enlarge the applicability of the functionals. This will be explained in subsections 5.5.2 and 5.5.3.

Besides functionals that depend explicitly on the density, we can also make use of the KS orbitals to generate more accurate functionals. This leads to terms in the functionals which depend on the density solely in an implicit way, via the KS orbitals. These functionals can, of course, only be used in the Hohenberg-Kohn theory combined with the KS scheme. The key advantage of such an approach is that the exchange part of the functional can be included in an exact manner. This leads to the class of the so-called hybrid functionals, which can be made totally self-interaction free (see subsection 5.5.4).

This section will be concluded with present-day efforts to enhance the asymptotic behavior of the functionals (subsection 5.5.5).

5.5.1 Thomas-Fermi and the Local Density approximation.

The Thomas-Fermi (TF) theory is based on a simple and well-studied physical system, the homogeneous electron gas. In the electron-gas system, the simultaneous limit of the number of particles \( N \to \infty \) and the volume \( V \to \infty \) is taken, under the condition that \( \frac{N}{V} \) remains constant (the thermodynamical limit). The TF model is based on the idea that a many-electron system can be decomposed into volume elements in which the density varies only slightly. In each of the volume elements, we apply the low-density expansion of the total-energy density for the homogeneous electron gas to derive an approximation for the \( \text{xc} \) functional. This expression can be found in e.g. [2] and reads

\[
\frac{E}{N} = \frac{3}{10} (3\pi^2 \rho_F)^{2/3} - \frac{3}{4\pi} (3\pi^2 \rho_F)^{1/3} + \ldots, \tag{5.78}
\]

where the (constant) Fermi-gas density is given by \( \rho_F = \frac{N}{V} \). In the TF approximation, the Fermi-gas density is replaced by the density \( \rho(\vec{r}) \), where \( \vec{r} \) is some characteristic position (e.g. the center) of the box in which the approximation is applied.

Actually, this technique was proposed in some very early density-functional models (late 1920s - 1930s) derived by Thomas [179], Fermi [180], Dirac [182], and von Weiszäcker [183]. Since the resulting functionals are very simple, they have been
5.5. Approximations to the exchange-correlation functional.

studied rather extensively within Hohenberg-Kohn theory. This resulted in a vast literature on the applications of the TF model and its extensions. For a general overview, the reader is referred to [130], [184], or [185].

In the TF theory, the kinetic-energy functional is approximated as [cf. first term in Eq. (5.78)]

\[ T_{TF}[\rho] = \frac{3}{10} (3\pi^2)^{2/3} \int d^3r \ \rho^{5/3}(r), \]  
(5.79)

while the two-electron energy is cast in the form of the direct Coulomb interaction

\[ W[\rho] \approx J[\rho] = \frac{1}{2} \int d^3r_1 \int d^3r_2 \ \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|}. \]  
(5.80)

This means that exchange and correlations effects are completely neglected! Since the external potential is generated by the nuclei in the system

\[ v(r) = -\sum_i \frac{Z_i}{r - r_i}, \]  
(5.81)

the total-energy functional [see e.g. Eq. (5.59)] is fully determined. When this functional is used in the Euler-Lagrange equation (5.36), the resulting density behaves erroneously in the asymptotic regions [103]: near nucleus \( i \) (which is at position \( \mathbf{r}_i \)) we obtain \( \rho(r) \sim |r - \mathbf{r}_i|^{-3/2} \), i.e. a singular behavior instead of a finite cusp, and at infinity we get (for neutral atomic systems) \( \rho(r) \sim r^{-6} \), instead of the expected exponential-type decay. The most striking failure, however, is that the radial density \( r^2 \rho(r) \) does not predict the typical shell-dependent oscillations. As a consequence, the resulting energies from the Hohenberg-Kohn theory using the TF model are only a rough estimate. Moreover, negative ions and molecules do not appear to be stable in the TF scheme (see [103]).

To improve this situation we could try to find an adequate approximation for the exchange (and correlation) effects. Dirac [182] proposed to incorporate exchange by means of [cf. second term in Eq. (5.78)]

\[ E_x[\rho] = -\frac{3}{4(\pi)^{1/3}} \int d^3r \ \rho^{1/3}(r) = \int d^3r \rho(r) \ \varepsilon^{unf}_x(\rho), \]  
(5.82)

which is then added to the direct Coulomb interaction \( J[\rho] \) to find the total two-body interaction approximation \( W[\rho] \approx J[\rho] + E_x[\rho] \). Most surprisingly, however, the resulting TFD scheme does not improve the behavior of the density nor the quality of the total energy [188]. It is noted that the so-called \( X_a \) (or the Hartree-Fock-Slater) method (see e.g. [130]) could be viewed as a crude approximation to the TFD model. We also refer to [194] for a review of rigorous results for a.o. the TF and TFD models.
Before discussing the higher-order terms in the expansion of the one-body density matrix in a general way (see next subsection), we first want to focus on a correction term that was proposed in 1935 already by von Weizsäcker [183]

\[ T_W[\rho] = \frac{1}{8} \int d^3r \frac{ \left| \nabla \rho(\mathbf{r}) \right|^2 }{\rho(\mathbf{r})}. \] (5.83)

This term is actually a correction for the TF kinetic energy and already takes into account part of the inhomogeneity effects.

With this correction, the TFDW total-energy functional becomes

\[ E_{TFDW} = T_TF[\rho] + \nu T_W[\rho] + J[\rho] + E_x[\rho] + \int d^3r \rho(\mathbf{r}) v(\mathbf{r}). \] (5.84)

The constant \( \nu \) can be adjusted depending on the system that is studied: in the original von Weizsäcker theory \( \nu = 1 \) is taken, which is a good approximation for rapidly varying densities. In the slowly varying regime, it is better to put \( \nu = 1/9 \) (see next subsection), while in intermediate regions \( \nu \) is chosen between 1 and 1/9, depending on the class of system at hand.

The TFDW functional results in a density with the correct asymptotic behavior on both sides (cusp condition and at infinity) and improves the predictions of the total energy. Also, negative ions are stable within this theory, provided that the maximum number of electrons does not exceed the total nuclear charge by more than the number of atoms in the molecule (at least within the TFW model, see [186]). However, within the pure Hohenberg-Kohn theory (i.e. without the KS scheme) even when the TFDW functional is used, the quantum-mechanical oscillatory structure of the radial density is not reproduced.

As indicated, if we use the TF(D) functionals in the Euler-Lagrange equation (5.36), the predictions for the total energy and the density are not satisfactory. On the other hand, the local density model is actually not that bad if the functionals are used within the self-consistent context of the KS scheme: the resulting energies and densities are better than the TF(D) approximation applied in the pure Hohenberg-Kohn theory, and the shell structure of the radial density is retrieved. The application of the local density model within a KS context is referred to as the Local Density Approximation (LDA). The improvement achieved by the LDA is even more pronounced if the spin degree of freedom is introduced explicitly in the scheme (the density \( \rho \) is then divided in a spin-up \( \rho^\uparrow \) and a spin-down \( \rho^\downarrow \) part), in which case the scheme is referred to as the Local Spin Density Approximation [LSD(A) for short]. The exchange part of the xc functional in the LDA scheme is modeled by Eq. (5.82) [131], while the correlation part consists of a more involved expression, although based on the electron gas as well. There is a vast amount of literature on this subject, but one of the most successful studies is the work of Ceperley and
Alder [189], who performed a quantum-Monte-Carlo calculation of the homogeneous electron gas. Adequate parametrizations were proposed by Voisko, Wilk, and Nusair [190] and by Perdew and Zunger [192]. Note that Voisko, Wilk, and Nusair (VWN) proposed several expressions for the correlation energy density. The parametrization that was based on the results of Ceperley and Alder is termed the VWN5 variant. Although the authors recommended use of this parametrization, another variant is used more frequently. It is not based on the results of quantum-Monte-Carlo calculations, but on the correlation energy of the homogeneous electron gas obtained in the Random Phase Approximation. Both parametrizations, however, perform similarly in most cases [191], although deviations have been reported [131]. More recently, Perdew and Wang [193] proposed an accurate and simple analytical representation of the electron-gas correlation energy by fitting to the results of Ceperley and Alder as well. The VWN and Perdew-Wang parametrizations are used frequently to include correlation effects in (a.o.) the LDA.

The different performance of the TFD and the LDA model illustrate the importance of describing the kinetic energy in an exact manner (to a large extent) as is done in the KS scheme. The kinetic-energy expansion proposed in the TFD scheme is clearly not good enough for use in the Euler-Lagrange equation. As opposed to this, the LDA results are comparable to or even better than the Hartree-Fock approximation and is successful in the determination of molecular properties such as equilibrium structures, harmonic frequencies, or charge moments [131]. The reason for this success is that the LDA-form for the xc hole (see section 5.2) originates from a physical system (the homogeneous electron gas) and therefore satisfies most of the important relations that hold for the exact hole (e.g. the sum rules, exchange-only hole negative everywhere, ...). However, LDA does a poor job in predicting energetical details such as bond energies (generally giving an overbinding, see e.g. [187] and [178]), which indicates that the terms in the expansion that are beyond the local density approximation are also important. In the next subsection, we will study the inhomogeneous terms in a more systematic way.

5.5.2 The Generalized Gradient Approximation (GGA).

Although the LDA is a good starting point that yields moderate accuracy, it is generally insufficient for chemical applications. Therefore, as long as LDA remained the sole practical approximation for DFT, the theory was used only in solid-state physics. This situation lasted until the 1980s, when the first successful extensions of the LDA were introduced. These corrections are based on two ideas.

The first idea was, evidently, to include inhomogeneities in the density by expanding the nondiagonal one-body density matrix in a Taylor series involving derivatives of the diagonal density. This idea was believed to give better results that LDA, based on the fact that gradients in the external potential \( \vec{\nabla} v(r) \) (which are assumed
zero in the LDA) correspond to gradients in the density $\hat{\nabla} \rho(\vec{r})$ (as follows from the Hohenberg-Kohn theorem). The term in the expansion which is of order zero corresponds to the LDA, while higher-order terms represent corrections to the LDA scheme. In that way, the functional expansion was extended to comprise gradients in the density, such that slowly varying densities could be described better. This technique to generate more advanced functionals is referred to as the Gradient Expansion Approximation (GEA). Note that schemes which go beyond the LDA are sometimes called nonlocal schemes. However, as the Taylor expansion in the density remains centered around a fixed point $\vec{r}$, the corresponding xc potential is still a local potential. This terminology only refers to the fact that extensions to the local density scheme are considered and should not be confused with the mathematical sense of ‘nonlocality’ in e.g. the Fock term [see Eq. (3.6) or Eqs. (4.2)-(4.3)], where the value of the exchange potential in point $\vec{r}$ depends on the value of the radial wave functions $P_\alpha(\vec{r}')$, for all $\vec{r}'$ in coordinate space.

When determining the gradient correction to the LDA, it turns out that the first order in $|\nabla \rho(\vec{r})|$ does not give a contribution [103]. For the kinetic-energy functional, we obtain to second order:

$$
T[\rho] = \frac{1}{2} \int d^3 r_1 \left[ \hat{\nabla}_{\vec{r}_1} \hat{\nabla}_{\vec{r}_2} \rho_1(\vec{r}_1, \vec{r}_2) \right] |_{\vec{r}_1 = \vec{r}_2} 
= -\frac{1}{2} \int d^3 r_1 \left[ \hat{\nabla}_{\vec{r}}^2 \rho_1(\vec{r}_1, \vec{r}_2) \right] |_{\vec{r}_1 = \vec{r}_2} 
\approx \int d^3 r \left\{ t^{(0)}(\vec{r}) + t^{(2)}(\vec{r}) \right\},
$$

(5.85)

where

$$
t^{(0)}(\vec{r}) = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}(\vec{r})
$$

(5.86)

is the TF approximation and

$$
t^{(2)}(\vec{r}) = \frac{1}{72} \frac{\left| \hat{\nabla} \rho(\vec{r}) \right|^2}{\rho(\vec{r})},
$$

(5.87)

is the von Weizsäcker correction [Eq. (5.83)], apart from an additional factor $\frac{1}{72}$.

The two-body interaction assumes the form

$$
W[\rho] \approx J[\rho] + E_x[\rho] \approx J[\rho] + \int d^3 r \left\{ e_x^{(0)}(\vec{r}) + e_x^{(2)}(\vec{r}) \right\},
$$

(5.88)

where the homogeneous term

$$
e_x^{(0)}(\vec{r}) = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{4/3}(\vec{r})
$$

(5.89)

is the Dirac expression for the exchange interaction in the LDA and the correction term is given by

$$
e_x^{(2)}(\vec{r}) = \frac{7}{432 \pi (3\pi^2)^{1/3}} \frac{\left| \hat{\nabla} \rho(\vec{r}) \right|^2}{\rho^{4/3}(\vec{r})},
$$

(5.90)
5.5. Approximations to the exchange-correlation functional.

derived by Herman, Van Dyke, and Ortenburger [195] and Sham [196]. We should note here that for finite systems, the terms in the expansion for the exchange energy of the order of four or beyond diverge, while the exchange potential itself already diverges at second order. Therefore, regularization techniques must be used to force the integrals in the expansion to convergence. This introduces some ambiguity in the coefficients of the terms in the perturbation series, as different regularization factors may produce other coefficients. Despite this indefiniteness, the gradient approximation up to second order results in improved total energies for atomic systems, as was pointed out by Herman et al. [195]-[197]. The success of the GEA functionals is limited though, and sometimes the predictions are even worse than in LDA [198]-[199]. This counterintuitive feature is explained by the fact that we have to truncate the gradient expansion at some order (e.g. second order). The truncation implies that the theoretical conditions satisfied by the exact xc hole will no longer hold for the extensions to the LDA scheme. This deficiency can result for some systems in a lower accuracy when the GEA is applied.

Therefore, the second idea of correcting the LDA, proposed by Perdew et al. ([200]-[203]), consists of introducing parameters to improve the predictive power of the functionals. The value of these parameters can be determined in two ways, depending on what kind of functional is desired. Either we can enforce the theoretical conditions on the functional by means of these parameters [204] or fit the functional to experimental data, allowing for a closer agreement with experiment. This kind of functionals is denoted as the Generalized-Gradient-Approximation (GGA) class. The GGA functionals are most popular in current applications of DFT and can be written in the general form

\[ E_{xc}^{GGA}[\rho] = \int d^3r \ f(\rho, \rho_\uparrow, \nabla \rho_\uparrow, \nabla \rho_\downarrow), \]  

(5.91)

where the spin polarization is introduced in the notation explicitly. As compared to the local spin-density approximation (LSD), GGA’s tend to improve total energies [203], atomization energies [203]-[206], energy barriers, and structural energy differences [207]-[211]. This effect is due to the fact that in the GGA, bonds in molecules are softened and expanded [206]. In all, GGA’s favor density inhomogeneities more than LSD does and corrects (sometimes overcorrects [212]) the latter scheme.

We know that only the xc functional has the role of the unique functional in the DFT-KS scheme. However, in practice, this functional is split into an exchange and a correlation part

\[ E_{xc}^{GGA}[\rho] = E_x^{GGA}[\rho] + E_c^{GGA}[\rho], \]  

(5.92)

and approximations are constructed separately for the two parts.
Focussing on the exchange part, we introduce the following notation

\[ E^{\text{GGA}}_x[\rho] = \sum_\sigma \int d^3r \: \rho_\sigma(\vec{r}) \: \epsilon^{\text{uni}}_x(\rho_\sigma) \: F_x(s_\sigma). \]  (5.93)

In this expression, we have introduce the energy density per particle for the uniform electron gas \( \epsilon^{\text{uni}}_x(\rho_\sigma) = -C_{x\sigma} \rho^{1/3}_\sigma(\vec{r}) \), where the coefficient \( C_{x\sigma} = \frac{2}{3} \) [compare with Eq. \( (5.82) \)]. The argument of the function \( F_x \) is called the reduced density gradient for spin polarization \( \sigma \):

\[ s_\sigma(\vec{r}) = \frac{\nabla \rho_\sigma(\vec{r})}{\rho^{1/3}_\sigma(\vec{r})}. \]  (5.94)

Depending on the expression proposed for the function \( F_x \), there are two important GGA-exchange functionals that can be distinguished [213]. The first one is developed by Becke [214] in 1988 and is denoted by B88

\[ F^{\text{B88}}_x(s_\sigma) = 1 + \frac{1}{C_{x\sigma} \left[ 1 + 6 \beta s_\sigma \text{Arccosh}(s_\sigma) \right]} \]  (5.95)

where the empirical parameter \( \beta = 0.0042 \) has been determined by a least-squares fit to the exactly known exchange energies of the noble-gas atoms He through Rn. Becke put forward this form to obtain the correct asymptotic behavior of the exchange-energy density \( \epsilon_x = \frac{1}{2} \sum_\sigma \epsilon^{\text{uni}}_x(\rho_\sigma) \) for a finite system, i.e. \( \epsilon_x(\vec{r}) \mid_{r \to \infty} = -1/(2r) \).

The second important GGA is actually a class of functionals, characterized by a rational function \( F_x \) in the reduced density gradient. This class of functionals is usually presented in a spin-independent form, where the enhancement factor \( F_x \) is defined in the expression

\[ E^{\text{GGA}}_x[\rho] = \int d^3r \: \rho(\vec{r}) \: \epsilon^{\text{uni}}_x(\rho) \: F_x(s), \]  (5.96)

with \( \epsilon^{\text{uni}}_x(\rho) = -\frac{3}{4} \left( \frac{3}{2} \rho \right)^{1/3} \). Within this class, we especially mention the form proposed by Perdew and Wang in 1986 [201]

\[ F^{\text{P86}}_x(s) = \left\{ 1 + 1.296 \left[ \frac{s}{(24\pi^2)^{1/3}} \right]^2 + 14 \left[ \frac{s}{(24\pi^2)^{1/3}} \right]^4 + 0.2 \left[ \frac{s}{(24\pi^2)^{1/3}} \right]^6 \right\}^{1/15}. \]  (5.97)

This functional is free of semiempirical parameters, just as the more recent implementation by Perdew, Burke, and Ernzerhof [215]

\[ F^{\text{PBE}}_x(s) = 1 + \kappa \frac{s}{1 + \frac{\kappa}{(24\pi^2)^{1/3}} s^2}, \]  (5.98)
where $\mu = 0.21951$ and $\kappa = 0.804$. These coefficients have been determined on theoretical grounds. Note that Becke also proposed this form in 1986 already [216], but with empirical parameters ($\mu = 0.235$ and $\kappa = 0.967$).

Concerning the correlation part of the xc GGA functional there is a variety of parametrizations as well. We mention in particular the parametrization of Perdew [199] who derived a correlation counterpart for the P86 exchange functional. This P86 correlation functional is often combined with the B88 exchange (5.95) to give rise to the popular BP86 xc functional. Furthermore, Perdew and Wang proposed an enhanced xc functional in 1991, which is denoted as PW91 [202]. This latter functional has been designed to obey a maximum number of theoretical conditions (see section 5.6). The PBE exchange functional (5.98) also has a correlation counterpart (derived by Perdew, Burke, and Ernzerhof [215] as well):

$$E^{\text{PBE}}_c[\rho, \rho_\downarrow] = \int d^3r \rho(r) [\epsilon^{\text{H}}_{\text{xc}}(r, \zeta) + H^{\text{PBE}}(r, \zeta, t)],$$  \hspace{1cm} (5.99)

where

$$r_s = \left(\frac{3}{4\pi \rho}\right)^{1/3},$$

$$\zeta = \rho_{\uparrow} - \rho_{\downarrow},$$

$$t = \frac{|\nabla \rho|}{2k_s \phi \rho},$$

$$\phi = \frac{1}{2}[(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}],$$

$$k_s = \frac{3}{2} \rho^2 \pi^{1/6},$$

$$H^{\text{PBE}} = \gamma \phi^3 \ln \left[ 1 + \frac{\beta}{\gamma} \left( \frac{1 + At^2}{1 + At^2 + A^2 t^4} \right) \right],$$

$$A = \frac{\beta}{\gamma} \left[ \exp\left( -\frac{\epsilon^{\text{H}}_{\downarrow}}{\gamma \phi^3} \right) - 1 \right]^{-1},$$  \hspace{1cm} (5.100)

and where $\gamma = 0.031091$, $\beta = 0.066725$. For the correlation part of the energy density of the uniform electron gas, $\epsilon^{\text{H}}_{\downarrow}$, the parametrization of Perdew and Wang [193] can be used. The functionals $E^{\text{PBE}}_x[\rho, \rho_\downarrow]$ [Eq. (5.98)] and $E^{\text{PBE}}_c[\rho, \rho_\downarrow]$ are derived on a totally ab initio basis by preserving and extending the correct formal properties of the LSD. Contrary to PW91, the PBE xc functional satisfies only the theoretical conditions that are energetically important instead of the maximum number possible (see also section 5.6).

One of the currently most popular correlation functionals was derived in 1988 by Lee, Yang, and Parr [90]. Unlike the functionals mentioned so far, this functional is
not derived from the uniform electron gas. It is based on an early attempt of Colle and Salvetti [217] to construct a density functional from the correlation energy for the helium atom. Because of the importance of the so-called LYP-functional in quantum-chemical applications, we present its form here [218]

\[
E_c^{LYP}[\rho_\uparrow, \rho_\downarrow] = -a \int d^3r \frac{4\rho_\uparrow(r)\rho_\downarrow(r)}{[1 + d\rho^{-1/3}(r)]\rho(r)} - ab \int d^3r \omega(\mathbf{r}) \left[ \rho_\uparrow(\mathbf{r})\rho_\downarrow(\mathbf{r}) \left[ \frac{2^{11/3}3^{1/3}C_F}{2} \rho_\uparrow(\mathbf{r})^{8/3}(\mathbf{r}) + \rho_\downarrow(\mathbf{r})^{8/3}(\mathbf{r}) \right] + \frac{47}{18} \delta(\mathbf{r}) + \frac{7}{18}\delta(\mathbf{r}) | \mathbf{\nabla}\rho(\mathbf{r}) |^2 - \frac{5}{2} - \frac{1}{18}\delta(\mathbf{r}) || \mathbf{\nabla}\rho_\uparrow(\mathbf{r}) |^2 + | \mathbf{\nabla}\rho_\downarrow(\mathbf{r}) |^2 - \delta(\mathbf{r}) - \frac{11}{9}\left[ \frac{\rho_\uparrow(\mathbf{r})}{\rho(\mathbf{r})} - \frac{1}{3}\rho(\mathbf{r}) \right] | \mathbf{\nabla}\rho_\uparrow(\mathbf{r}) |^2 + \frac{2}{3}\rho_\uparrow(\mathbf{r}) | \mathbf{\nabla}\rho_\downarrow(\mathbf{r}) |^2 + \frac{2}{3}\rho_\downarrow(\mathbf{r}) | \mathbf{\nabla}\rho_\uparrow(\mathbf{r}) |^2 \right],
\]

(5.101)

where

\[
\omega(\mathbf{r}) = \frac{\rho^{-1/3}(\mathbf{r})}{1 + d\rho^{-1/3}(\mathbf{r})} e^{-c\rho^{-1/3}(\mathbf{r})}, \quad \delta(\mathbf{r}) = c\rho^{-1/3}(\mathbf{r}) + \frac{d\rho^{-1/3}(\mathbf{r})}{1 + d\rho^{-1/3}(\mathbf{r})}, \quad C_F = \frac{3}{10}(3\pi^2)^{2/3}.
\]

(5.102)

The parameters \( a = 0.04918, \ b = 0.132, \ c = 0.2533, \) and \( d = 0.349 \) were obtained by Colle and Salvetti from a fit to the He atom. The form presented here differs from the original one reported by Lee, Yang, and Parr in [90] in that the \( \nabla^2\rho \) has been eliminated by a partial integration, which is numerically preferable. The LYP correlation functional can be combined with Becke’s 1988 exchange functional to give rise to the powerful BLYP xc functional, which has been used with great success in a variety of applications.

It is important to note that all of the common correlation functionals are based on systems (the uniform electron gas or the helium atom) that include only dynamical correlation effects. This part of the correlation is directly connected to the electron-electron repulsion in the hamiltonian. It represents the mutual influence of the electrons on their propagation through the medium and is of short-range nature. Another, more long-range contribution to the correlation energy is called the nondynamical or static part. In a noninteracting framework (like Hartree-Fock or Kohn-Sham) it is related to the fact that in certain circumstances the ground-state Slater determinant is not a good approximation to the true ground state, because there are other Slater determinants with comparable energies. It has been argued that the approximative exchange functionals reproduce the sum of exchange and nondynamical correlation (see e.g., [219]-[222]). In this way, the combined exchange and correlation include both dynamical and nondynamical correlation. In passing,
we also remark that the generalized gradient expansions do not have an explicit dependence on the particle number \( N \). Therefore, the functional derivative of the total energy does not exhibit the required discontinuity when \( N \) passes through an integer, as imposed by the discontinuity of the chemical potential (see section 5.3).

To assess the quality of the various functionals, it is costumary to study systems that belong to the so-called \textit{G2 reference set} [223], which is a compilation of highly accurate experimental data on atomization energies, ionization potentials, and electron and proton affinities of more than a 100 first-row and second-row atomic and molecular systems. Recently, a new, more extended and more accurate reference set has been constructed that will become the next standard test set: the \textit{G3/99 reference set} [224]. In this work, the discussion will be restricted to benchmarks against the \( G2 \) set. In general, it is possible to obtain an accuracy of about five to seven kcal/mole (0.008 - 0.011 a.u.) with respect to the \( G2 \) data set using current GGA xc functionals. The absolute average error of e.g. the BPW91 functional (B88 combined with PW91) is about 5.7 kcal/mole (0.009 a.u.).

It is clear that the GGA functionals are quite successful in reducing the error of the LDA scheme. However, since applications of DFT become ever more demanding, the strive to improve the accuracy of the functionals is still continuing. In the next two subsections, we will describe these attempts. In the first approach (subsection 5.5.3), more terms in the expansion (5.91) are taken into account, while the second one (subsection 5.5.4) tries to describe the exchange part in an exact way.

5.5.3 The Meta-Generalized Gradient Approximation (meta-GGA).

The xc functionals mentioned in the preceding sections are explicit functionals in the density. In the KS scheme, however, we also have access to s.p. orbitals, allowing to construct functionals that depend explicitly on the KS orbitals. These functionals are still functionals of the electron density in an implicit way due to the correspondence between the KS orbitals and \( \rho \). In this subsection and particularly in the next subsection, we will discuss a few examples of orbital-dependent functionals.

The \textit{Meta-Generalized Gradient Approximation (meta-GGA)} extends the integrand in Eq. (5.91) with information such as the Laplacian \( \nabla^2 \rho_\sigma \) or the \textit{kinetic-energy density} of the occupied KS orbitals

\[
\tau_\sigma (\vec{r}) = \frac{1}{2} \sum_{\alpha (\text{occ.})} | \nabla \phi_{\alpha \sigma} (\vec{r}) |^2 .
\]

The total kinetic-energy density \( \tau = \tau_\uparrow + \tau_\downarrow \) for spin-compensated systems \((\rho_\uparrow = \rho_\downarrow)\) has the following second-order gradient expansion in terms of the density [225] [see also Eqs. (5.86) and (5.87)]

\[
\tau_{GGA}(\vec{r}) = \frac{3}{10} (3 \pi^2)^{2/3} \rho^{5/3}(\vec{r}) + \frac{1}{72} \frac{| \nabla \rho(\vec{r}) |^2}{\rho(\vec{r})} + \frac{1}{6} \nabla^2 \rho(\vec{r}).
\]
In this way, we see that introduction of \( \tau(\vec{r}) \) in the functional implies that terms beyond the GGA are taken into account in the density expansion. As argued by Becke ([226], [227]), \( \tau(\vec{r}) \) is a natural ingredient of both the exchange and the correlation energy. Extensions of the GGA class that incorporate the kinetic-energy density are referred to as meta-GGA functionals. In fact, this class of functionals was already proposed in the 1980's ([200],[228]) and preceded most GGA functionals. However, the meta-GGA’s only received much attention when the quest for more accuracy reached the limits of the GGA class ([227], [229]). Meta-GGA’s can achieve high accuracy, as illustrated by the constructions in [206], [227], and [229]-[231] which are based upon fits to chemical data.

We here present briefly the meta-GGA of Perdew et al. [229], which has been derived along similar lines as the PBE xc functional. The exchange part of their meta-GGA is written as (for a spin-unpolarized density \( \rho \))

\[
E_{x}^{\text{MGGAP}}[\rho] = \int d^3r \, \rho(\vec{r}) \xi^\text{unif}_x(\rho) F_x(\rho, \vec{\nabla}\rho, \tau),
\]

where \( \xi^\text{unif}_x(\rho) = -\frac{3}{4\pi}(3\pi^2 \rho)^{1/3} \) is again the exchange energy per particle for the uniform electron gas. For the form of the enhancement function \( F_x \), Perdew et al. proposed something similar to Eq. (5.98), namely

\[
F_x(p,q) = 1 + \kappa - \frac{\kappa}{1 + x(p,q)},
\]

where

\[
x(p,q) &= \frac{10}{81} + \frac{146}{2025}q^2 - \frac{73}{405}p + \left[ D + \frac{1}{\kappa} \left( \frac{10}{81} \right)^2 \right]p^2,
\]

\[
p &= \frac{|\nabla \rho|^2}{4(3\pi^2)^{2/3} \rho^{8/3}} = \left[ \frac{s}{(24\pi^2)^{1/3}} \right]^2,
\]

\[
q &= \frac{3\tau}{2(3\pi^2)^{2/3} \rho^{8/3}} - \frac{9}{20} - \frac{p}{12}.
\]

The parameter \( \kappa \) was set to 0.804, the largest value which ensures that the Lieb-Oxford bound (see section 5.6) is satisfied. The parameter \( D = 0.113 \), on the other hand, was fit to minimize the mean absolute error in the atomization energies of some molecules composed of atoms of the first and second column of the Periodic System.

The corresponding meta-GGA correlation energy functional retains the correct formal properties of the PBE correlation functional, such as the correct slowly varying limit and the finite limit for \( E_c[\rho_\lambda] \) under uniform scaling as the scale parameter \( \lambda \to \infty \) (see section 5.6). Its form is

\[
E_{c}^{\text{MGGAP}}[\rho_\uparrow, \rho_\downarrow] = \int d^3r \, \rho c_{cGGA}^{\text{unif}}(\rho_\uparrow, \rho_\downarrow, \vec{\nabla}\rho_\uparrow, \vec{\nabla}\rho_\downarrow) \left[ 1 + C \left( \frac{\sum \tau^W}{\sum \tau^\sigma} \right)^2 \right]
\]
5.5. Approximations to the exchange-correlation functional.

\[-(1 + C) \sum_\sigma \left( \frac{\tau_\sigma^W}{\tau_\sigma} \right)^2 \rho_\sigma \epsilon_c^{GGA}(\rho_\sigma, 0, \nabla \rho_\sigma, 0),\]  

(5.108)

where \( \epsilon_c^{GGA} = \epsilon_c^{\text{nlf}} + H^{PBE} \) is the PBE correlation energy per electron [Eq. (5.99)] and where

\[\tau_\sigma^W = \frac{1}{8} \frac{|\nabla \rho_\sigma|^2}{\rho_\sigma},\]  

(5.109)

is the Weizsäcker kinetic-energy density. This form for the correlation functional is self-interaction free: it vanishes for the density of any one-electron system, for any value of the parameter \( C \). This parameter is set to 0.53 to give surface correlation energies for jellium in close agreement with the predictions of the PBE functional [229]. We note that, contrary to the PBE functional, this meta-GGA has two fitted parameters (\( C \) and \( D \)) and only one parameter (\( \kappa \)) which was derived \textit{ab initio}.

As stated above, the meta-GGA's can obtain an accuracy beyond the reach of the GGA's. The meta-GGA (5.105)+(5.108) performs better than the PBE functional: in benchmark calculations of the atomization energies of 20 small molecules, the mean absolute error of the meta-GGA is 3 kcal/mole (0.005 a.u.), which is more than a factor of 2 better than the PBE functional and a factor of 10 than LSD. The meta-GGA constructed by Filatov and Thiel on semi-empirical grounds [230] also gives a mean absolute error of 3 kcal/mole (0.005 a.u.).

Becke introduced two very accurate meta-GGA's that also belong to the hybrid class of functionals (discussed in the next subsection): the kinetic-energy density is present along with a term incorporating a fraction of exact exchange. The first hybrid meta-GGA [232] obtains an average absolute error of about 2 kcal/mole (0.003 a.u.) and is referred to as the B1B95 functional. It was introduced by Becke in 1996 and includes only one parameter. The second hybrid meta-GGA of Becke was proposed in 1998 [227] and generates a very good fit to the G2 data [overall average (rms) error of 2.59 kcal/mole or 0.004 a.u.].

Finally, we mention a meta-GGA xc functional developed by Van Voorhis and Scuseria [231] which performs equally well as the ones of Becke. It is denoted as the VSXC functional and is particularly interesting because there was no need to include exact-exchange mixing to arrive at a high accuracy.

In spite of the accuracy of the meta-GGA class, the hybrid functionals which are discussed in the next subsection remain the most popular functionals if high accuracy is desired. This is probably due to the fact that, though the accuracy of meta-GGA and hybrid functionals is very similar, the former functionals sometimes suffer from numerical problems, which trouble a robust implementation [233]-[236].

5.5.4 Hybrid functionals.

Besides the meta-GGA functionals discussed in the previous subsection, there is another powerful class of orbital-dependent functionals, namely the \textit{hybrid functionals}. 


This group has been developed throughout the 1990s and have enjoyed an unprecedented success [237]. The key idea on which hybrids are founded is that it is possible to evaluate the exchange part of the functional exactly by means of the Fock expression [see chapters 3 and 4 or Eq. (5.111) below]. Of course, within the KS scheme, the KS orbitals are used in the Fock expression, but due to the similarity of the KS and the Hartree-Fock orbitals, the prediction for the exchange energy should not differ much from the Hartree-Fock value. With the exchange part known exactly, we only have to find an accurate form for the correlation functional:

\[
E_{xc}[\rho] = E_{x}^{\text{exact}}[\rho] + E_{c}[\rho].
\]  

(5.110)

The exact-exchange expression is (|\Phi_0\rangle is the ground-state Slater determinant constructed from the KS orbitals)

\[
E_{x}^{\text{exact}}[\rho] = \langle \Phi_0 | \hat{W} | \Phi_0 \rangle - \frac{1}{2} \int d^3r_1 \int d^3r_2 \rho(\vec{r}_1)\rho(\vec{r}_2) \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}
\]

\[
= -\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \delta_{m_{i},m_{j}} \int d^3r_1 \int d^3r_2 \frac{\phi_i^{K\Sigma}(\vec{r}_1)\phi_j^{K\Sigma}(\vec{r}_2)\phi_i^{K\Sigma}(\vec{r}_1)\phi_j^{K\Sigma}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}.
\]  

(5.111)

This approach performs well in atomic systems, but does not improve the description of the chemical bond as obtained with the GGA functionals. To give an idea of the accuracy, we note that against the G2 reference set, a DFT-KS calculation involving exact exchange-only [i.e. in Eq. (5.110) we neglect the correlation part] has a mean absolute error of 78 kcal/mole (0.124 a.u.). Adding an approximate correlation functional we can reduce the error to about 32 kcal/mole (0.051 a.u.). One of the advantages of including exact exchange is that, just as in Hartree-Fock, the hamiltonian does not suffer from spurious self-interaction introduced by the Hartree term [Eq. (5.51)]. Within DFT, it depends entirely on the xc functional whether the self-interaction will be cancelled and therefore, self-interaction-free functionals have received attention relatively early (see e.g. [238]). However, we note that the accuracy of hybrids taking into account full exact exchange is a lot worse than the performance of GGA where both the exchange and correlation part are approximated. This points out that in the GGA a cancellation of errors between the exchange and the correlation part takes place. Yet, taking into account a fraction of exact exchange leads to good results, as we will now discuss.

Becke pursued this idea to include exact exchange in the functionals and proposed a variety of hybrid functionals in a series of papers ([239]-[241]). The development of these functionals is based on the adiabatic-connection method (ACM), which was discussed in section 5.4. It was illustrated that the true xc energy can be derived from an integration over the adiabatic-connection curve involving the xc hole (\( \lambda \) is...
the coupling-strength parameter):

\[
E_{xc} = \int_0^1 d\lambda \int d^3r_1 \int d^3r_2 \frac{\rho(\vec{r}_1) h^\lambda_{xc}(\vec{r}_1; \vec{r}_2)}{2 | \vec{r}_1 - \vec{r}_2 |}
\]

\[
E_{xc} = \int_0^1 d\lambda E_{xc}^\lambda
\]

(5.112)

The \( \lambda = 0 \) side of the integrand in Eq. (5.112) is known exactly. The KS system consists of noninteracting fermions and therefore the only contribution to \( E_{xc}^{\lambda=0} \) is the exact exchange \( E_{xc}^{\text{exact}}[\rho] \), evaluated with the KS orbitals. For the other limit (\( \lambda = 1 \)), correlation interactions are important as well and therefore this limit is not known exactly. It can however be approximated by one of the (exchange-)correlation functionals introduced before.

Becke used the simplest approximation possible to perform the integration in Eq. (5.112) and proposed the \textit{half-and-half combination} of exact exchange and the LDA form for the xc functional \( E_{xc}^{\lambda=1} \) [239]:

\[
E_{xc}^{HH} = \frac{E_{xc}^{\lambda=0} + E_{xc}^{LDA}}{2} = \frac{E_{xc}^{\text{exact}} + E_{xc}^{LDA}}{2}
\]

(5.113)

For the correlation part of \( E_{xc}^{LDA} \), Becke proposed to use the parametrization of Perdew and Wang [193]. Given the absolute average error of about 6.5 kcal/mole (0.010 a.u.) with respect to the G2 data set, the adiabatic-connection method seems a promising route to derive functionals. However, in the \( E_{xc}^{HH}[\rho] \) functional, the uniform electron gas limit is not obtained, which is a disturbing failure from a theoretical perspective. Also, while atomization energies are good, ionization potentials and proton affinities are extremely poor [240]. Therefore, further development along the lines of the adiabatic-connection method was required.

With these considerations in mind, Becke introduced weights to monitor the different contributions to the integral [240]

\[
E_{xc}^{B3} = E_{xc}^{LSD} + a(E_{xc}^{\text{exact}} - E_{xc}^{LSD}) + bE_{xc}^{B88} + cE_{xc}^{PW91},
\]

(5.114)

where the parameters were fitted to some energetic data of the G2 set (which resulted in \( a = 0.20, b = 0.72, \) and \( c = 0.81 \)). Of course, the absolute average error referred to the G2 set is reduced significantly due to the fit (to about 2-3 kcal/mole or 0.003-0.005 a.u.), but this is no guarantee that the functional will perform equally well for systems outside the reference set. In Eq. (5.114), \( E_{xc}^{PW91} \) stands for the 1991 gradient correction for correlation of Perdew and Wang [202].

Based on the B3 functional, Stephens et al. [242] suggested a hybrid that has become one of the most powerful xc functionals. It performs very well in a large variety of chemical applications. This so-called \textit{B3LYP functional} uses the LYP correlation functional [see Eq. (5.101)] instead of the PW91 functional, while the
value of the three empirical parameters is left unchanged. Also, the LDA part of the correlation (e.g. the Vosko-Wilk-Nusair parametrization) is not fully taken into account, but by a fraction 1 - c:
\[
E_{xc}^{\text{BLYP}} = (1 - a)E_{xc}^{\text{LSD}} + aE_{xc}^{\text{exact}} + bE_{xc}^{\text{B88}} + cE_{xc}^{\text{LYP}} + (1 - c)E_{xc}^{\text{LSD}}.
\] (5.115)

The average unsigned G2 error for this functional is only little above 2 kcal/mole (0.003 a.u.), i.e. already very close to the limit of chemical accuracy, which is 1 kcal/mole or 0.0016 atomic units.

Finally, we note that Becke proposed a more intricate approximation to the integral (5.112) in 1997 [241]:
\[
E_{xc}^{\text{B86}} = E_x^{\text{GGA}} + E_c^{\text{GGA}} + c_{xc}^{\text{exact}} E_{xc}^{\text{exact}},
\] (5.116)

where the amount of exact exchange \( c_{xc}^{\text{exact}} \) was set to 0.20. We note that on purely theoretical grounds a fraction of exact exchange \( c_{xc}^{\text{exact}} \approx 0.25 \) seems advisory, as was shown by Perdew, Ernzerhof, and Burke in 1996 [243] and by Burke, Ernzerhof, and Perdew in 1997 [244]. In Eq. (5.116), the \( E_x^{\text{GGA}} \) and the \( E_c^{\text{GGA}} \) components are expanded in a power series of the density and the reduced density gradient:

\[
E_x^{\text{GGA}} = \sum_{\sigma} \int d^3 r \, e_{xc}^{\text{unif}}(\rho_\sigma) \, g_{xc}(s_{\sigma}^2),
\]
\[
e_{xc}^{\text{unif}}(\rho_\sigma) = -\frac{3}{2} \left( \frac{3}{4\pi} \rho_\sigma \right)^{1/3} \rho_\sigma,
\]
\[
g_{xc}(s_{\sigma}^2) = \sum_{i=0}^{M} c_{x,i} (u_{xc})^i,
\]
\[
u_{xc}(s_{\sigma}^2) = \frac{\gamma_{xc} s_{\sigma}^2}{1 + \gamma_{xc} s_{\sigma}^2},
\]
\[
\gamma_{xc} = 0.004
\] (5.117)

for the exchange and

\[
E_c^{\text{GGA}} = \sum_{\sigma} E_{c}^{\sigma\sigma} + E_{c}^{\uparrow\downarrow},
\]

\[
E_{c}^{\sigma\sigma} = \int d^3 r \, e_{c}^{\text{unif}}(\rho_\sigma) \, g_{c}^{\sigma\sigma}(s_{\sigma}^2),
\]
\[
g_{c}^{\sigma\sigma}(s_{\sigma}^2) = \sum_{i=0}^{M} c_{c,i} (u_{c\sigma\sigma})^i,
\]
\[
u_{c\sigma\sigma}(s_{\sigma}^2) = \frac{\gamma_{c} s_{\sigma}^2}{1 + \gamma_{c} s_{\sigma}^2},
\]
\[
\gamma_{c} = 0.2,
\]

\[
E_{c}^{\uparrow\downarrow} = \int d^3 r \, e_{c}^{\text{unif}}(\rho_{\uparrow}, \rho_{\downarrow}) \, g_{c}^{\uparrow\downarrow}(s_{\text{avg}}^2),
\]
5.5. Approximations to the exchange-correlation functional.

\[ g^{\uparrow\uparrow}_{\alpha\beta}(s_{\text{avg}}^2) = \sum_{i=0}^{M} c^{\uparrow\uparrow}_{\alpha\beta} (u_{\alpha\beta})^i \]

\[ u_{\alpha\beta}(s_{\text{avg}}^2) = \gamma_{\alpha\beta}^\uparrow \frac{s_{\text{avg}}^2}{(1 + \gamma_{\alpha\beta}^\uparrow s_{\text{avg}}^2)} \]

\[ \gamma_{\alpha\beta}^\uparrow = 0.006, \]

\[ s_{\text{avg}}^2 = \frac{1}{2}(s_1^2 + s_2^2) \]  

(5.118)

for the correlation part. We also introduced the correlation-energy density per unit volume for the parallel-spin \((e_{\text{corr}}^{\text{unif}}})\) and the opposite-spin \((e_{\text{corr}}^{\text{unif}}})\) uniform electron gas. These can be calculated from the total LSD correlation-energy density \(e_{\text{corr}}^{\text{unif}}})\) by the trick of Stoll et al. [245]

\[ e_{\text{corr}}^{\text{unif}}}(\rho_\sigma) = e_{\text{corr}}^{\text{unif}}}(\rho_\sigma, 0), \]

\[ e_{\text{corr}}^{\text{unif}}}(\rho_\uparrow, \rho_\downarrow) = e_{\text{corr}}^{\text{unif}}}(\rho_\uparrow, \rho_\downarrow) - e_{\text{corr}}^{\text{unif}}}(\rho_\uparrow, 0) - e_{\text{corr}}^{\text{unif}}}(\rho_\downarrow, 0). \]  

(5.119)

Remark that we denote the energy density \textit{per unit volume} by \(e\) and the energy density \textit{per particle} by \(\rho\); the relation between the two is \(e = \rho \epsilon\).

Becke truncated the expansions (5.117)-(5.118) at second order \((M = 2)\), which resulted in 10 linear parameters \((\text{including } e_{x}^{\text{exact}})\) that were optimized with respect to the G2 set in an elaborate fitting procedure. The resulting absolute average G2 error is about 1.8 kcal/mole \((0.0029 \text{ a.u.})\). It was argued by Becke that this is about the maximum accuracy which is possible with conventional GGA functionals for exchange and correlation, mixed with a fixed amount of exact exchange. Reparametrizations were made by Schmidt and Becke (to include an extension of the G2 set used by Becke) [246] and by Hamprecht et al. [247]. The latter reparametrization is referred to as B97-1. Another extension by Hamprecht et al. consists of truncating the expansions only at fourth order \((M = 4)\). It does not include exact exchange in the functional \((e_{x}^{\text{exact}} = 0)\) and is therefore no hybrid functional. In all, 15 parameters are to be fitted. Hamprecht et al. used this increased flexibility of the functional to introduce more observables in the fit, namely nuclear gradients for molecules and accurate \(\text{xc}\) potentials derived from high-level densities. This so-called HCTH functional will be discussed further in chapter 6.

Finally we note that Perdew, Burke, and Ernzerhof ([243], [244]) proposed a number of parameter-free hybrid functionals of the general form

\[ E_{\text{xc}}^{\text{hybrid}} = E_{\text{xc}}^{\text{GGA}} + \epsilon_{x}^{\text{exact}} (E_{x}^{\text{exact}} - E_{x}^{\text{GGA}}). \]  

(5.120)

The amount of exact exchange was put to \(\epsilon_{x}^{\text{exact}} = 0.25\). If the PBE functional is chosen as the GGA component of the hybrid functional, we arrive at the PBE1PBE (which is sometimes referred to as the PBE0 functional). It can be shown that this \textit{ab initio} functional is competitive with the most reliable, empirically parameterized present-day functionals [248].
Summarizing, it was demonstrated in this subsection that the introduction of a fraction of exact exchange turns out to be beneficial. However, recent developments indicate that including exact exchange is not always necessary to arrive at accurate functionals. The HCTH functional is one example of such a functional. Another example was mentioned at the end of the previous subsection: the VSVX meta-GGA of Van Voorhis and Scuseria yields accuracies comparable to those of the hybrid functionals but without including exact exchange. Van Voorhis and Scuseria [231] therefore concluded that the apparent need to include an exact exchange part with current density functionals is merely a relic of the relatively poor quality of exchange functionals that have been introduced in the past. Nevertheless, to the present day, none of the more recent functionals mentioned above is able to compete in popularity with the established BP86, BLYP, or B3LYP functionals.

5.5.5 Exchange-correlation functionals with exact asymptotic behavior.

Current xc functionals are quite accurate in describing the region of space where the electron density is substantial, which suffices for every-day applications (such as energetic predictions) in quantum chemistry. However, as the applicability of DFT is extended, properties become of interest for which the asymptotic region of the density and the xc potential is important. A deficient asymptotic behavior of the density will result in an altered energy spectrum of the KS system. Therefore, all quantities that are related to e.g. excitation energies of the KS system such as the electron affinity or the response of a system to electromagnetic probes (e.g. polarizabilities and infrared transitions in molecules) will be affected.

There are actually two problems concerning the asymptotic region of present-day popular xc functionals. First, it is obvious that the xc potential should have a \(-\frac{1}{r}\) behavior. However, the majority of the approximative potentials decrease in an exponential way and are consequently less attractive than the exact one at large \(r\). The second problem is more of an abstract nature and concerns the choice of the additive constant in the xc potential. The problem is related to the extension of DFT that deals with systems involving of a fractional number of electrons. If one considers an ensemble-based extension of DFT and its KS formulation to non-integer electron number, one can extend the definition of the xc potential as the functional derivative of the underlying exact xc energy functional, now valid for integer and non-integer electron number. This seemingly removes the freedom of the additive constant by relating it to the total energy, but on second thought this is not correct: at integer electron number the derivative is ill-defined, and the exact xc potential jumps by a system-dependent constant when taking the limit to an integer from the electron-deficient or electron-abundant side (the so-called derivative discontinuity, [149]). So at integer electron number the exact KS potential is again defined up to an additive constant, and it can be shown (see e.g. Ref. [249, 252]) that an xc
5.5. Approximations to the exchange-correlation functional.

potential which corresponds to taking the limit from the electron-deficient side has
the following asymptotic behavior:

$$\lim_{r \to \infty} \psi_{xc}(r) = \frac{1}{r} + \mathcal{I} + \epsilon_{\text{ion}}^{KS},$$

(5.121)

where \( \mathcal{I} \) is the first ionization energy and \( \epsilon_{\text{ion}}^{KS} \) is the energy of the highest occupied KS level. Expression (5.121) evidently follows from the KS equations when it is realized that the asymptotic behavior of the highest occupied orbital is \( \lim_{r \to \infty} \varphi_{\text{ion}}^{KS}(r) \sim r^{-2} \kappa^{2} + \mathcal{I} \kappa^{2} e^{-\kappa r} \), with \( \kappa = (2\mathcal{I})^{1/2} \) and where \( Z_N \) is the total charge of all nuclei present in the system (this system is assumed to be finite and to have an \( N \)-electron nondegenerate ground state [133]). By using an argument of Perdew et al. [149], it can be shown easily [178] that in the exact density-functional formalism the highest occupied KS eigenvalue gives the ionization energy of the system (i.e. Koopmans’ theorem is valid \( \mathcal{I} = -\epsilon_{\text{ion}} \)). As a consequence, the electron-deficient limit of the exact xc potential vanishes at infinity. Note that the relation between \( \epsilon_{\text{ion}} \) and \( \mathcal{I} \) has been studied extensively and that there has been and is still some debate on this topic. We refer to V. Russier [250] for a careful analysis of the discussion. Functionals that do not incorporate the derivative discontinuity are called continuum xc functionals, as they are continuous with respect to variations in the number of electrons [158]. Earlier discussions on these topics can also be found in [133] (asymptotic behavior of xc potentials) and [251] (constant shift of the potential). None of the currently implemented functionals describes this derivative discontinuity, and it is doubtful whether any analytical formulation will be able to include this phenomenon.

Yet, the system-dependent shift becomes more and more of interest in the development of new functionals or the improvement of established ones. Since the shift will be studied in the next section, we elaborate here upon its origin and properties. It can be shown that the hardness of an electronic system (i.e. \( \frac{dE}{dN} = A \), where \( A \) is the electron affinity) provides an upper limit for the constant shift (see e.g. [252] and [253]). To illustrate this, we consider the total energy \( E \) of an electron system as a function of the number of electrons. It is clear that this function consists of a series of straight-line segments, where the derivative is discontinuous at the integer numbers ([103], [130]): see Fig. 5.1.

Focussing on the part of the diagram with \( N - 1, N, \) and \( N + 1 \) electrons, we have that

$$\frac{\partial E}{\partial N}(N - \delta) = E_N - E_{N-1} = -\mathcal{I}$$

$$\frac{\partial E}{\partial N}(N + \delta) = E_{N+1} - E_N = -A,$$

(5.122)

where \( 0 < \delta < 1 \) and where \( \mathcal{I} \) and \( A \) are respectively the first-ionization energy and the electron affinity of the \( N \)-electron system. We now relate these derivatives to
Figure 5.1: Total energy of many-electron system in function of a varying number of electrons.

the KS eigenvalues [149]. We can induce a variation in the number of electrons by
varying the occupation numbers $n_i$ of the KS orbitals. This implies that

$$
\frac{\partial E}{\partial N}(N-\delta) = \frac{\partial E}{\partial n_N}(N-\delta)
$$

$$
\frac{\partial E}{\partial N}(N+\delta) = \frac{\partial E}{\partial n_{N+1}}(N+\delta).
$$

(5.123)

Combined with Janak’s theorem [254], $\frac{\partial E}{\partial n_i} = e_i^{KS}$ (where $e_i^{KS}$ is KS eigenvalue $i$),
we arrive at

$$
e_N^{KS}(N-\delta) = -I
$$

$$
e_N^{KS}(N+\delta) = -A.
$$

(5.124)

From this result, we obtain that in the limit of $\delta \to 0$

$$
e_N^{KS}(N) + e_{N+1}^{KS}(N) = -(I + A),
$$

(5.125)

as was derived by Perdew and Levy [255]. Since we know that $e_N^{KS}(N) \leq e_{N+1}^{KS}(N)$,
it follows that

$$
e_N^{KS}(N) \leq -\frac{I + A}{2},
$$

(5.126)

and keeping in mind that $\lim_{r \to \infty} v_{xc}^N(r) = v_{xc}^N(\infty) = I + e_N^{KS}(N)$, we find

$$
v_{xc}^N(\infty) \leq \frac{I - A}{2}.
$$

(5.127)
This will be illustrated with a numerical example in the next chapter.

To elaborate more upon the effect of the discontinuous jump, let us consider the KS equations for the highest occupied orbital in systems with \( N - \delta \) and \( N + \delta \) electrons, where \( \delta \to 0^+ \). The external potential and the potential corresponding to the Coulomb repulsion as well as the orbitals themselves are continuous with respect to the number of electrons. The KS equations are therefore [compare with Eq. (5.56)]

\[
\begin{align*}
\left[ -\frac{1}{2} \nabla^2 + v(N) + v_J(N) + \lim_{\delta \to 0} v_{xc}(N - \delta) - \lim_{\delta \to 0} \epsilon_{K}^{S}(N - \delta) \right] \phi_{N}^{KS} &= 0 \\
\left[ -\frac{1}{2} \nabla^2 + v(N) + v_J(N) + \lim_{\delta \to 0} v_{xc}(N + \delta) - \lim_{\delta \to 0} \epsilon_{K}^{S}(N + \delta) \right] \phi_{N+1}^{KS} &= 0.
\end{align*}
\] (5.128)

Using Eq. (5.124), we obtain the following expression for the derivative discontinuity

\[
\lim_{\delta \to 0} v_{xc}(N + \delta) - \lim_{\delta \to 0} v_{xc}(N - \delta) = (I - A) - \frac{1}{2} \left( \frac{\nabla^2 \phi_{N}^{KS}}{\phi_{N}^{KS}} - \frac{\nabla^2 \phi_{N+1}^{KS}}{\phi_{N+1}^{KS}} \right)
\]

\[
= C. \tag{5.129}
\]

From this we deduce that there will be no kinetic contribution to the derivative discontinuity if the ground state of the negative ion can be obtained by putting an electron in the highest occupied KS orbital of the neutral atom: \( \phi_{N}^{KS} \) and \( \phi_{N+1}^{KS} \) coincide (see also [253]). This is typically the case for open-shell systems. In this way, we can also understand that for the open-shell case, the asymptotic constant \( v_{xc}^{\infty}(\infty) \) will equal the hardness \( \frac{E-A}{2} \) exactly: the difference between the first-ionization energy and the electron affinity is the sole contribution to the derivative discontinuity.

With the discontinuity in mind, a more appropriate definition of the xc potential corresponding to integer \( N \) seems the average of the electron-deficient and the electron-abundant limiting potentials

\[
v_{xc}^{N}(r) = \frac{1}{2} \left[ \lim_{\delta \to 0} v_{xc}^{N+\delta}(r) + \lim_{\delta \to 0} v_{xc}^{N-\delta}(r) \right]. \tag{5.130}
\]

It should be noted that due to the mixing with exact exchange, the hybrid functionals partly take into account the two problems in the asymptotic regime. The asymptotic form of the exact exchange indeed behaves as \(-\frac{1}{r}\), but because in most cases only a fraction \( \alpha \) of exact exchange is considered, the asymptotic behavior is not totally correct (see also [256]). Also, the introduction of some Hartree-Fock exchange leads to a discontinuity of the potential if the number of electrons increases through an integer [257].

There have been several studies over the years that tried to correct the asymptotic behavior of existing potentials or to derive new xc functionals which lead to
Chapter 5. Density Functional Theory

potentials with the correct behavior at infinity. One of the first attempts was made by van Leeuwen and Baerends [258], but their potential cannot be derived from a functional and does not take into account the derivative discontinuity. As mentioned before, Hamprecht et al. [247] introduced exact xc potentials derived from \textit{ab initio} calculations in the fitting procedure of their HCTH functional (see also next chapter), along with energetic data. In the fit, they allowed for a system-dependent shift of the exact potentials to incorporate the derivative discontinuity. In fact, it has been shown by Handy et al. ([252], [259]) that without this constant shift a considerable loss in accuracy results for the prediction of the total energy. However, because of the nature of the gradient expansion which defines their HCTH functional [see Eqs. (5.117) and (5.118)], the corresponding potential first of all vanishes, and, second, does so in a wrong way (i.e. not with a $-1/r$ behavior). Therefore, Tozer and Handy [249] corrected the HCTH potential according to Eq. (5.121), which resulted in the HCTH(AC) potential. A drawback of their correction procedure is that the potential can no longer be cast easily in the form of the derivative of an xc functional (this functional is needed in \textit{e.g.} the expression for the total energy). As a consequence, none of the xc functionals proposed so far takes into account properly the derivative discontinuity of the corresponding potential. The asymptotic correction has also been applied to hybrid functionals by Allen and Tozer [260], but no overall improvement over the results obtained with the HCTH(AC) was achieved. For other studies in this field, we refer to Chermette et al. [261].

To conclude this section on the approximations of the exact xc functional, we note that in practical calculations a trade-off has to be made between accuracy and numerical cost. The classification of the approximate xc functionals into LDA, GEA, GGA, meta-GGA, and hybrid classes is sometimes referred to as \textit{Jacob's ladder}: a functional that appears on a higher rung of the ladder belongs to a more advanced class and yields a larger accuracy (approaching chemical accuracy, \textit{i.e.} 1 kcal/mole or 0.0016 a.u.), but implies a higher numerical payload.

5.6 Exact relations for the exchange-correlation functional.

As mentioned in section 5.3, DFT does not indicate how density functionals should be constructed. However, a number of useful relations that are obeyed by the exact xc functional can be derived [167], [262]-[271]. Although it is not necessary for a functional to satisfy (all of) these relations to give good results, the rules can provide a foothold when new functionals are derived or old ones are enhanced.

In Table 5.1, we list the most important rules and indicate for some of the functionals that have been discussed whether they satisfy the condition or not. For the LDA xc functional, we took the Dirac exchange functional Eq. (5.82), combined with the Perdew-Wang parametrization of the homogeneous electron gas [193] for
the correlation part. Another choice for the correlation part, the Vosko-Wilk-Nusair parametrization, is discussed separately.

The first group of properties (1 - 3) concerns the exchange and correlation hole that are related to the xc functional. As was explained in section 5.2, the exchange hole $\rho_x(\vec{r},\vec{r}')$ is negative everywhere in coordinate space and integrates to $-1$. This indicates that the exchange hole removes exactly one electron from the density distribution. The correlation hole $\rho_c(\vec{r},\vec{r}')$ integrates to zero and consequently does not have a fixed sign.

The second set of conditions (4 - 6) provides bounds on the functionals. Note that condition 6 is known in the literature as the Lieb-Oxford bound.

Many of the remaining relations we mention here use the concept of scaling, which means that a scaling factor $\lambda$ is introduced by which the spatial variables $\vec{r}_1, \ldots, \vec{r}_N$ are multiplied. The scaled density $\rho_\lambda$ is defined as $\rho_\lambda(\vec{r}) = \lambda^3 \rho(\lambda \vec{r})$. This definition is such that both the scaled and the unscaled density integrate to the same number of particles $N$. Also, the scaled wave function $\chi_\lambda(\vec{r}_1, \ldots, \vec{r}_N)$ (assumed normalized and antisymmetric) reads

$$\chi_\lambda(\vec{r}_1, \ldots, \vec{r}_N) = \lambda^{3N/2} \chi(\lambda \vec{r}_1, \lambda \vec{r}_2, \ldots, \lambda \vec{r}_N). \quad (5.131)$$

We note that the kinetic energy $\hat{T}$ and the two-body Coulomb interaction $\hat{W}$ scale in different ways (see e.g. [264]):

$$\langle \Psi_\lambda | \hat{T} | \Psi_\lambda \rangle = \lambda^2 \langle \Psi | \hat{T} | \Psi \rangle, \quad \langle \Psi_\lambda | \hat{W} | \Psi_\lambda \rangle = \lambda \langle \Psi | \hat{W} | \Psi \rangle, \quad (5.132)$$

where $| \Psi \rangle$ is a normalized antisymmetric $N$-body wave function.

It is important to note, however, that for the kinetic-energy and two-body interaction functionals we cannot derive equalities as in Eq. (5.132): they only obey the inequality (for $\lambda \neq 1$) [264]

$$T[\rho_\lambda] + W[\rho_\lambda] < \lambda^2 T[\rho] + \lambda W[\rho], \quad (5.133)$$

with $T[\rho_\lambda] + W[\rho_\lambda] = \min_{\Psi_\lambda \rightarrow \rho_\lambda} \langle \Psi_\lambda | \hat{T} + \hat{W} | \Psi_\lambda \rangle$ [cf. Eq. (5.39)], and where

$$T[\rho] = \langle \Psi[\rho] | \hat{T} | \Psi[\rho] \rangle, \quad W[\rho] = \langle \Psi[\rho] | \hat{W} | \Psi[\rho] \rangle, \quad (5.134)$$

with $| \Psi[\rho] \rangle$ the wave function that yields the density $\rho$ and has minimal expectation value for $\langle \hat{T} + \hat{W} \rangle$.

The scaling relations (5.132) are important because they can be used to derive stringent relations for the exact xc functional (potential), some of which are discussed below.
In this respect, we mention a scaled version of the Lieb-Oxford bound, which can be found in [262]:
\[
\lim_{\lambda \to 0} \frac{1}{\lambda} E_{xc}[\rho_{\lambda}] = \inf_{\psi \rightarrow \rho} \left( \langle \Psi | \hat{W} | \Psi \rangle - \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} \right) \geq -c \int d^3 r \rho^{4/3}(r),
\]
(5.135)

where \( 1.43 < c < 1.68 \).

The third set of relations (7 - 10) comprises the uniform scaling relations of the exchange and correlation functionals separately [264]-[265]. This kind of properties poses restrictions on which combinations of the density and the density derivative can be present in the exact functional form. Note that condition 8 is equivalent to the condition \( E_{c}[\rho_{\lambda}] > \lambda E_{c}[\rho], \lambda > 1 \). Also, we remark that the PW91 functional diverges to \( \infty \) in the limit of condition 9. However, the less stringent condition \( \lim_{\lambda \to 0} E_{c}[\rho_{\lambda}] = -\infty \) is satisfied. The PW91 functional can be modified to obey the more limiting condition 9 as well [262]. We point out condition 10 too, for which it was derived in [272] that
\[
\lim_{\lambda \to 0} \frac{1}{\lambda} E_{c}[\rho_{\lambda}] = \text{constant},
\]
(5.136)

where, in its most stringent form, the constant value is less than zero and greater than \( -J[\rho] \), with \( J[\rho] \) being the direct Coulomb interaction energy [see Eq. (5.48)]. As reported in [271], the correlation functionals PW91, PBE, VWN, and LYP considered in Table 5.1 satisfy this condition even in its most restrictive form.

The fourth group (11 - 18) also deals with scaling relations, but with scaling in a nonuniform way; the density is only stretched out in one or two spatial dimensions (temporarily, \( x \) does not stand for \( \vec{r} \sigma \) nor for exchange here, but is just the first coordinate of \( \vec{r} \)):
\[
\rho_{\lambda}^{(x)}(\vec{r}) = \lambda \rho(\lambda x, y, z), \quad \rho_{\lambda}^{(y)}(\vec{r}) = \lambda^2 \rho(\lambda x, \lambda y, z).
\]
(5.137)

It should be pointed out that the derivation of the scaling relations involves some important assumptions such as the premise that a Taylor series in \( \lambda \) or \( 1/\lambda \) exists for the functional under study. An overview of the scaling relations and their derivation can be found in [270]. The scaling conditions of Table 5.1 (both uniformly and nonuniformly) are mentioned in their most stringent form.

The fifth group of requirements (19 - 21) for the exact functional concerns the long-range behavior (for finite systems) of the exchange potential and the local exchange energy per electron \( \epsilon_e \), which is defined by (see also section 5.5.2) \( E_x[\rho] = \int d^3 r \rho(\vec{r}) \epsilon_e(\rho(\vec{r}), \nabla \rho(\vec{r}), \nabla^2 \rho(\vec{r}), \ldots) \). Also, the short-range limit of the exchange and the correlation potential is addressed. For the case of condition 19 it is noted
that the B88 functional only satisfies this condition for an exponentially decaying density, for \textit{e.g.} a Gaussian density we have that \( e_{\text{B88}}^x (r) \to -\frac{1}{r} \) \cite{273},

It can be demonstrated \cite{274} that concerning the long-distance region, a GGA functional that includes no derivatives of the density beyond first order cannot simultanously satisfy the correct behavior for the xc potential \((-1/r)\) and the local exchange energy per electron \([-1/(2r)]\). Fortunately, it turns out that including the second-order derivative (in an appropriate way \cite{273}) allows for a triple advantage: the resulting (meta-)GGA not only satisfies the long-range behavior of both the xc potential and the local exchange energy per electron, we furthermore have that the xc potential remains finite at the nuclei of the system \cite{275}\textendash\cite{276}. The important role of the second-order derivative was also indicated by Engel and Vosko \cite{277}.

The last group of conditions (22 - 23) deals with the limit for a homogeneous density (LDA) and for a slowly varying density (second-order GEA).

Note that the functional of Perdew and Wang \( E_{\text{PW91}}^{\text{xc}} \) satisfies the largest number of conditions. It was already mentioned in section 5.5.2 that this functional has been constructed to obey a maximum number of theoretical conditions.

This survey of the theoretical conditions on the xc functional concludes the general chapter on DFT. In the next chapter, it will be discussed how the Green’s function calculations of chapters 3 and 4 can be used to provide the approximate functionals in DFT with an \textit{ab initio} basis.
Table 5.1: Some properties of the exact xc functional and assessment of approximative functionals. For the correlation part of $E_{xc}^{LDA}$, the parametrization of Perdew and Wang [193] was assumed. In condition 6, the constant $c$ is bracketed by $1.43 < c < 1.68$.

<table>
<thead>
<tr>
<th>Property</th>
<th>$E_{xc}^{LDA}$</th>
<th>$E_{xc}^{WF}$</th>
<th>$E_{xc}^{PL}$</th>
<th>$E_{xc}^{SS}$</th>
<th>$E_{xc}^{wA}$</th>
<th>$E_{xc}^{FP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\rho_2(\vec{r}, \vec{r}') \leq 0$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2. $\int d^3r' \rho_2(\vec{r}, \vec{r}') = -1$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3. $\int d^3r' \rho_2(\vec{r}, \vec{r}') = 0$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4. $E_y[\rho] &lt; 0$</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5. $E_c[\rho] \leq 0$</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>-</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>6. $E_y[\rho], E_{xc}[\rho] \geq -c \int d^3r \rho^{1/3}(\vec{r})$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7. $E_z[\rho] = \lambda E_{xc}[\rho]$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8. $E_c[\rho] &lt; \lambda E_{xc}[\rho], \lambda &lt; 1$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>9. $\lim_{\lambda \to \infty} E_y[\rho_\lambda] = finite$</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>-</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>10. $\lim_{\lambda \to 0} E_y[\rho_\lambda] = finite$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>11. $\lim_{\lambda \to \infty} E_{xc}[\rho_\lambda] = finite$</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12. $\lim_{\lambda \to 0} E_{xc}[\rho_\lambda] &gt; -\infty$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13. $\lim_{\lambda \to \infty} \frac{1}{\lambda} E_{xc}[\rho_\lambda] &gt; -\infty$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14. $\lim_{\lambda \to 0} \frac{1}{\lambda} E_{xc}[\rho_\lambda] &gt; -\infty$</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15. $\lim_{\lambda \to \infty} \lambda E_{xc}[\rho_\lambda] = finite$</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>-</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>16. $\lim_{\lambda \to 0} \frac{1}{\lambda} E_{xc}[\rho_\lambda] = 0$</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>-</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>17. $\lim_{\lambda \to \infty} E_{xc}[\rho_\lambda] = 0$</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>-</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>18. $\lim_{\lambda \to 0} \frac{1}{\lambda} E_{xc}[\rho_\lambda] = finite$</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>-</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>19. $v_x(\vec{r}) \to -1/2r, r \to \infty$</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20. $v_z(\vec{r}) \to -1/r, r \to \infty$</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>21. $v_x(\vec{r}), v_z(\vec{r})$ finite for $r \to 0$</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>22. LDA limit for constant $\rho$</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>23. GEA limit for slowly varying $\rho(\vec{r})$</td>
<td>-</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>-</td>
<td>N</td>
</tr>
</tbody>
</table>
Chapter 6

Ab initio study of DFT based on the Green’s function formalism.

6.1 Introduction.

In the previous chapter the Density Functional Theory (DFT) was introduced. It allows for a fast treatment of Coulomb systems and is able to tackle intricate molecules because it solves the many-body problem by means of Schrödingerlike equations for single-particle orbitals, the Kohn-Sham equations. The two-body exchange and correlation effects are folded into the one-body exchange-correlation (xc) potential, for which no exact explicit expression is known. Since DFT proves only the existence of a unique and universal xc potential, but does not give any clues on how to construct it, a large number of xc functionals have been proposed on semi-empirical grounds.

Although these functionals are quite successful, they are constructed by a fit to experimental data, which is less satisfying from a theoretical point of view. Semi-empirical constructions are actually unsatisfactory in two ways [229]. First, the xc functional should be derived from quantum mechanics, without the need for an excessive number of parameters fitted to experimental data. Universal functionals should be based on universal principles. Second, semi-empirical functionals typically fail for the uniform electron gas [which is the one limit in which the GGA and meta-GGA functional forms (see previous chapter) can be exact] and also for solids. Furthermore, as present-day applications of DFT become more challenging, there is a growing interest in more advanced functionals. Therefore, a systematic way to improve functionals based on ab initio grounds is desirable from both a theoretical as well as a practical viewpoint.

Many commonly used xc functionals describe correctly merely the region in space where the electron density is substantial. As a consequence, the asymptotic behavior of the corresponding potential \((-\frac{1}{r})\) can be erratic. This is not problematic when only the total energy is to be predicted since the asymptotic region is not impor-
tant for this observable. Yet, other quantities such as atomic electron affinities and properties related to the response to an electromagnetic field (e.g., polarizabilities) depend on the asymptotic behavior of the density in a crucial way [249]. In section 5.5.5, several efforts were mentioned that tried to improve the functionals in the asymptotic region. One way is to include (fractions of) exact exchange in the functionals, while fitting the parameters of the functional to energetic data only (see Refs. [239]-[241]). Another route is to include not only energetics in the fit but also xc potentials derived in an ab initio approach (see e.g., [252]). The latter approach will be discussed in this chapter. The idea is to calculate the one-body electron density using a very accurate method such as Monte-Carlo, configuration interaction, coupled-cluster, or Green’s function techniques. In these methods, the amount of correlations embodied in the electron density can be increased systematically e.g. by taking into account more interacting configurations (which of course increases the numerical cost). It has even been suggested to use experimental electron densities [278].

In chapters 3 and 4, calculations based on self-consistent Green’s function theory were presented for atomic systems. More particularly, we solved the Dyson equation self-consistently up to second order in the two-body interaction. The resulting one-body density extracted using this method incorporates a major part of the correlations present in the atomic systems. If we want to make a connection with DFT, we need to find the xc potential that DFT would require to describe the same atomic density. This is the so-called inversion problem and over the years several algorithms to solve this problem have been developed (see e.g., [279]-[287]), though they are sometimes restricted to a few small systems like helium, beryllium, or neon atoms. Amongst the more general schemes we mention in particular the density-response scheme (Refs. [282] and [269]), and the method of Zhao, Morrison, and Parr (ZMP, see Ref. [286]). The former technique generates the Kohn-Sham potential by solving an integral equation for the inverse response function of the Kohn-Sham system, while in the latter the noninteracting kinetic energy is minimized under the restriction that the Kohn-Sham density equals the input density. These methods have a solid physical foundation, but they are rather intricate and can be difficult to implement in a numerically stable way.

In this chapter, we tackle the inversion problem in coordinate-space using a new scheme, that is simple, numerically robust and applicable to any atomic input density. The basic principles underlaying the scheme are quite general and we therefore expect the scheme to work for systems without spherical symmetry as well. The procedure, which uses an iterative local update of the exchange-correlation potential, is similar to the procedure proposed in Ref. [258] but seems to be numerically more stable. As indicated above, we will apply this algorithm to electron densities obtained from Green’s function calculations. As will be discussed, the potentials generated by the scheme show the correct asymptotic behavior and the characteristic intershell peaks.
6.2 Inverse-problem algorithm.

We can use the generated potentials in fitting procedures for existing or new functionals, along with energetic data resulting from the Green’s function calculation which produced the input densities. In this way, a microscopic study of current functionals can be performed, providing an ab initio basis for DFT. This may result in model potentials with e.g. improved asymptotic behavior such that some properties, like polarization quantities, are predicted with larger accuracy. Efforts along this path can lead to more fundamental guidelines to derive functionals, thereby hopefully increasing the predictive power of DFT. We illustrate this procedure in a preliminary study of a recent functional proposed by Hamprecht et al. (the HCTH functional, see Ref. [247] and previous chapter). The quest for functionals that are derived ab initio is very popular nowadays. In this respect, we also mention the recent efforts of Bartlett et al. who generated a new orbital-dependent correlation functional based on second-order perturbation theory (see Ref. [288] and references therein).

The outline of this chapter is as follows. In section 6.2, the inversion algorithm is presented which determines the xc potential corresponding to a given input one-body density. Though this section is mainly numerical in nature, we point out the underlaying physical principles of the algorithm where possible. In section 6.4, we discuss the potentials found for some closed-shell atoms (He, Be, Ne, Mg, and Ar) and open-shell atoms (B, C, N, O, and F) using the densities as derived from our self-consistent Green’s function scheme. In section 6.5, two applications of the generated potentials are discussed, a.o. the microscopic analysis of the HCTH functional (see subsection 6.5.2). Finally, a possible generalization of the Kohn-Sham scheme based on the Green’s calculations in chapters 3 and 4 is sketched in section 6.6.

6.2 Inverse-problem algorithm.

The algorithm will be presented in a spin-restricted form: the spin-polarized version of the expressions can be found by simply adding the spin index \( \sigma \). As throughout this work, atomic units will be used.

For a given N-electron input density \( \rho^{eJ}(\vec{r}) \), the inversion problem consists of determining the unique local potential \( v_b(\vec{r}) \) that generates this density through the Kohn-Sham (KS) equations. Stated otherwise, we must have that

\[
\rho^{eJ}(\vec{r}) = \rho^{KS}(\vec{r}) = \sum_{i=1}^{N} |\phi_i^{KS}(\vec{r})|^2,
\]

where the \( N \) Kohn-Sham orbitals in Eq. (6.1) are the lowest-energy solutions of

\[
\left[-\frac{1}{2}\nabla^2 + v_b(\vec{r})\right] \phi_i^{KS}(\vec{r}) = \epsilon_i^{KS} \phi_i^{KS}(\vec{r}).
\]
In general, the effective potential of the KS system reads
\[
v_{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + v_J(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}),
\]
and consists of the external potential \(v(\mathbf{r})\), the Hartree repulsion
\[
v_J(\mathbf{r}) = \int d^3 r' \frac{\rho^{\text{KS}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},
\]
and the xc potential \(v_{\text{xc}}(\mathbf{r})\). We restrict our study to spherically symmetric atomic systems without additional external fields, i.e. \(v(\mathbf{r}) = -Z/r\), where \(Z\) is the atomic number. As a consequence, only the radial degree of freedom is relevant.

In our algorithm the inversion problem is solved using an iterative scheme. All terms in \(v_{\text{eff}}(\mathbf{r})\) that are known exactly are kept fixed over the iterations, i.e. only the xc potential is varied. The Hartree potential in Eq. (6.4) is evaluated using the input density \(\rho^{\text{ref}}(r)\). We initialize the xc potential by means of the Dirac potential [182]:
\[
v_{\text{xc}}^{(0)}(r) = -\left[\frac{3}{\pi} \rho^{\text{ref}}(r)\right]^{\frac{1}{3}}.
\]
The Dirac potential provides a reasonable approximation for the exchange part, which is the dominant contribution to the xc potential.

Suppose that we have the xc potential of iteration \(n\), then we solve the KS equations (6.2) corresponding to this potential in coordinate space and construct the KS electron density:
\[
\rho^{\text{KS}(n)}(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i^{\text{KS}(n)}(\mathbf{r})|^2.
\]
The xc potential of the next iteration is found by applying the following correction:
\[
v_{\text{xc}}^{(n+1)}(r) = v_{\text{xc}}^{(n)}(r) + \alpha r \beta \left[\rho^{\text{KS}(n)}(r) - \rho^{\text{ref}}(r)\right] + \left[T^{\text{KS}}_{n} - T_{\text{ref}}\right] f(r).
\]
The last term in Eq. (6.7) contains the ionization energy \(T^{\text{KS}}_{n}\), where \(\epsilon_{\text{ion}}^{\text{KS}(n)}\) is the energy of the highest occupied Kohn-Sham orbital in iteration \(n\). The ionization energy \(T_{\text{ref}}\) is determined unambiguously by the asymptotic behavior of the input density. Its role will be explained in the next paragraphs, along with the parameters \(\alpha\) and \(\beta\) and the function \(f(r)\).

With the update (6.7) for the xc potential, the KS equations are solved anew and this process is repeated until convergence. As the convergence criterion we impose a condition on the integrated density deviation,
\[
4\pi \int dr \ r^2 \left| \rho^{\text{KS}(n)}(r) - \rho^{\text{ref}}(r) \right| < \Delta,
\]
6.2. Inverse-problem algorithm.

with $\Delta = 10^{-5}$. For the open-shell inversion, the convergence condition is imposed on both spin densities separately and $\Delta_s = 5 \times 10^{-6}$.

The effective KS potential $v_s$ is only determined up to an additive constant by Eqs. (6.1-6.2), and can be fixed completely by the requirement that it vanishes at infinity. Due to the fact that our initial guess (the Dirac potential) in Eq. (6.5) vanishes asymptotically, and due to the structure of the update scheme Eq. (6.7), this requirement is automatically fulfilled for the converged solution as well.

Any reasonable electron density $\rho^{ref}(r)$ can be used as input in the algorithm. However, in order to obtain good asymptotic properties for the xc potential, it is required that the input density itself has the correct exponential-type decay. For a neutral atom with nondegenerate groundstate we have that [133] (see also section 5.5.5),

$$\rho^{ref}(r) \sim e^{-2\kappa r^{-2}(\frac{1}{\kappa}-1)}, \quad (6.9)$$

where $\kappa = (2I_{ref})^{1/2}$. From this expression, we clearly see that the ionization energy is in principle determined by the asymptotic region of the input density $\rho^{ref}$. We employed the highly correlated densities as obtained from our Green’s function calculations, but the scheme can also be applied to densities found by other methods (e.g. quantum-Monte-Carlo calculations).

Let us now have a closer look at the update scheme in Eq. (6.7). The physical significance of the first correction term is that if the KS density of iteration $n$ is larger than the reference density $\rho^{ref}(r)$ in some region in space, then the xc potential of the next iteration will become more repulsive in that region. In this way, the KS density of iteration $n + 1$ should be closer to the input density.

In expression (6.7), the value of the (positive) parameters $\alpha$ and $\beta$ is in general not crucial for the final converged form of the potential, but can have an important influence on the number of iterations required to reach convergence. The parameter $\alpha$ determines the overall weight of the local correction to the xc potential due to the difference between the KS and input density. The parameter $\beta$ increases the weight of the large-$r$ region, for which the correction would otherwise be very small.

We obtained convergence for $\alpha$ ranging from 0.5 to 3.5 a.u., while the value of $\beta$ could be varied between zero and three, at least for all closed-shell atoms in this study. In the open-shell case, the tuning of the $\beta$ parameter turned out to be more delicate, however, and it was found that its value should preferably be selected around $\beta \approx 2$ for B and C, while we obtained good results with $\beta \approx 1.5$ for N, O, and F.

It is clear that the first correction term is related to the idea that a minor change in the one-body density induces a linear-response reaction in the effective KS potential. The exact expression for this response is nonlocal,

$$\delta v_s(\vec{r}) = \int d^3r' \chi^{-1}(\vec{r}, \vec{r}') \delta \rho(\vec{r}'), \quad (6.10)$$
Figure 6.1: Comparison of convergence properties of the present method in Eq. (6.7) and the method of van Leeuwen and Baerends (LB) of Eqs. (6.14-6.15). The neon HF density was used as input. Full line: present method. Dot-dashed line: LB method. Upper panel: integrated density deviation of Eq. (6.8) versus iteration number. Lower panel: KS ionization energy (in atomic units) versus iteration number.

where the response function of the KS system is defined as (for a closed-shell system):

\[ \chi(r_i, r'_i) = 2 \sum_{i(\text{occ.})} \sum_{j(\text{unocc.})} \frac{\phi_i^{KS}(r_i)\phi_j^{KS}(r'_i)\phi_i^{KS}(r_i')\phi_j^{KS}(r'_i)}{\epsilon_i^{KS} - \epsilon_j^{KS}} + (\text{c.c.}) \]  

(6.11)

The factor 2 arises because of the double degeneracy of each orbital in a closed-shell system. In the open-shell case, the spin degree of freedom is to be introduced and the response function assumes the form

\[ \chi_\sigma(r, r') = \sum_{i(\text{occ.})} \sum_{j(\text{unocc.})} \frac{\phi_i^{KS}(r)\phi_j^{KS}(r')\phi_i^{KS}(r)\phi_j^{KS}(r')}{{\epsilon_i^{KS} - \epsilon_j^{KS}}} + (\text{c.c.}) \]  

(6.12)

In this case, the effective potential in Eq. (6.10) also becomes spin dependent.

Eqs. (6.10-6.11) have been used [267, 282, 269] to find the effective KS potential by iteratively determining the inverse \( \chi(r_i, r'_i)^{-1} \) of the response function. The
determination of the inverse $\chi(r, r')^{-1}$ of the response function can only be done in a restricted space, which does not include constant functions (corresponding to zero KS eigenvalues). This means that the KS potential is determined up to some constant. Our algorithm also determines the xc potential in this restricted space. As indicated before, however, due to the fact that our initial guess [the Dirac potential of Eq. (6.5)] vanishes asymptotically, the arbitrary shift of the potential is put to zero. If the inverse $\chi^{-1}$ is calculated using finite basis-set expansions for the potential and/or the KS orbitals, severe problems may arise [267, 282]. These are not encountered in the grid-based method of Ref. [269], where it was found, however, that spurious oscillations appear in the converged potential if the input density does not have the correct asymptotic behavior. This indicates the sensitivity of the potential even to spatial regions where the density is very small, as will be further discussed in section 6.4.

The second correction term in Eq. (6.7) is not strictly necessary to obtain convergence to an xc potential with correct asymptotic behavior (see section 6.4). Without the second term, however, the highest occupied KS eigenvalue may be somewhat off the value for $I_{\text{ref}}$ corresponding to the tail of the input density. This is due to the fact that in the asymptotic region, the first correction term (even with the extra factor $r^\beta$) is small, and a very large number of iterations would be required to ob-
tain an accurate matching for the ionization energies. To alleviate this problem, we added the second term: it ensures that the absolute value of the energy of the highest occupied KS level coincides with the ionization energy \( I_{\text{ref}} \). The factor \( f(r) \) in the second term has the following form:

\[
f(r) = \theta(1 - r) r^\gamma + \frac{\theta(r - 1)}{r^\delta}
\]  

(6.13)

The step functions \( \theta(x) \) allow for a continuous transition between the two terms at a distance of one atomic unit. Again, the parameters \( \gamma \) and \( \delta \) only affect the speed of convergence of the scheme; we only require their value to be positive. In our calculations, we used \( \gamma \approx 5 \) for the closed-shell atoms and \( \gamma \approx 1 \) for the open-shell cases. The parameter \( \delta \) can be taken \( \delta \approx 3 \) in all cases. Both parameters, however, can be varied within a wide range without affecting the final form of the converged potential.

6.3 Numerical test of the scheme.

The inversion algorithm as presented in the previous section was first tested at the exchange-only level, using Hartree-Fock (HF) input densities calculated in coordinate space (see chapters 3 and 4). Note that the coordinate-space HF scheme automatically leads to the correct asymptotic behavior of Eq. (5.121). As an example, we show in Fig. 6.2 the effective exchange potential corresponding to the neon HF density (see dashed line in 6.3). It is seen to be extremely close to the Optimized Effective Potential (OEP) exchange-only potential of Ref. [280], which is the local potential that generates orbitals which minimize the HF energy functional.

It is also interesting to compare the iterative procedure in Eq. (6.7) with the one introduced by van Leeuwen and Baerends [258], henceforth called the LB scheme. The LB scheme for solving the inversion problem uses a different local update,

\[
\psi^{(n+1)}_{el}(r) = U^{(n)}(r) \psi^{(n)}_{el}(r),
\]

(6.14)

\[
U^{(n)}(r) = \frac{\rho^{[n]}_{KS}(r)}{\rho^{[n]}_{ref}(r)},
\]

(6.15)

where \( \psi_{el}(r) = \psi_H(r) + \psi_{ee}(r) \) the electron-electron part of the KS potential. Note that in the original scheme appearing in [258],

\[
\psi^{(n+1)}_s(r) = \frac{\rho^{[n]}_{KS}(r)}{\rho^{[n]}_{ref}(r)} \psi^{(n)}_s(r),
\]

(6.16)

obviously some printing error has occurred; it is defined in the unstable direction since the total KS potential \( \psi_s(r) \) is usually negative. The stable direction would involve the local update factor \( \rho^{[n]}_{ref}(r)/\rho^{[n]}_{KS}(r) \). In later papers by the Amsterdam
6.3. Numerical test of the scheme.

Figure 6.3: Hartree-Fock (dashed), Dyson(2) (dot-dashed) and corrected Dyson(2) (full line) density for neon.

group it is clear that they advocate updating, according to Eq. (6.15), the electron-electron part of the KS potential only, which is a positive quantity. The update factor $U(r) = \rho_{KS}(r)/\rho_{ref}(r)$ must be kept within reasonable bounds, e.g. by imposing [258]

$$1 - \epsilon \leq U(r) \leq 1 + \epsilon,$$

(6.17)

where $\epsilon \sim 0.05$, or by considering [268]

$$U(r) = \frac{\rho_{KS}(r) + a}{\rho_{ref}(r) + a},$$

(6.18)

where $a \sim 0.5$ atomic units.

Note that a local update scheme in terms of a multiplicative factor with fixed sign [like the ratio of the $n$th iteration density and the target density in Eq. (6.15)] is problematic in the sense that it cannot change the local sign of the unknown potential from its initial estimate. While this hardly matters for electron systems - one can isolate the $v_{el}$ part which has a fixed sign - it can be unworkable in other problems, e.g. in nuclear physics. So on general grounds an iterative scheme like Eq. (6.7), where the unknown potential can change its local sign during iterations, is to be preferred.
Another practical remark is that the LB method seems to be much more sensitive to the initial estimate for the xc potential, e.g., using the Dirac expression (6.5) we failed to achieve convergence for the neon Hartree-Fock density in the LB scheme. We did obtain convergent results using (see Ref. [209]) an initial estimate

\[ v_{xc}^{(0)}(r) = - \left[ \frac{3}{\pi} \rho_{\text{ref}}(r) \right]^\frac{1}{3} + 2e^B_{\text{ref}}(\rho_{\text{ref}}(r), |\nabla \rho_{\text{ref}}(r)|), \] (6.19)

where \( e^B_x \) is the Becke gradient correction to the exchange energy density [214]; the latter term imposes the correct asymptotic \(-1/r\) behavior of the initial estimate. Note that in scheme presented in this work (6.7) this behavior is built up automatically during iterations, even with an initial estimate like Eq. (6.5) which is exponentially decaying.

In the upper panel of Fig. 6.1 we compare, for the case of the neon HF density, the convergence speed of the density deviation in Eq. (6.8) for the LB scheme and the scheme we proposed in this chapter. For the LB scheme expression (6.18) was used with \( a = 3 \) a.u.; smaller values of \( a \), or the use of expression (6.17), both led to instabilities in the recursion scheme. For the present scheme (6.7) parameter values \( \alpha = 3.5, \beta = 1, \gamma = 5, \delta = 3 \) have been taken. In both cases the initial estimate (6.19) was used. The present scheme seems to converge faster for this case. Moreover, the ionization energy consistent with the input HF density for Ne, \( I_{\text{ref}} = 0.850 \) a.u., is reached very rapidly, as can be seen in the lower panel of Fig. 6.1. The LB scheme yields an ionization energy which is approaching the correct one, but convergence is slow.

### 6.4 Results.

The inversion algorithm was next applied at the full exchange plus correlation level using input densities resulting from Green’s function calculations in which Dyson’s equation is solved self-consistently up to second-order in the two-body interaction. As was demonstrated in chapters 3 and 4, this so-called Dyson(2) scheme incorporates the most important correlations in many-electron systems, providing a good reproduction of e.g. ionization energies, electron affinities, and total energies.

The Dyson(2) scheme uses a HF basis set, which is constructed by solving the HF equations in coordinate space [Dyson(1) scheme]. Inherent to the method is a discretization of the continuum part of the energy spectrum by adding a parabolic potential wall to the HF hamiltonian. This wall is switched on only at a large distance (see Tables 3.8 and 4.1) from the nucleus, where the one-body density is already in its asymptotic regime. Although the energetic aspects of the calculations are not influenced by this discretization scheme, the parabolic potential does affect the asymptotic region of the density. In view of the sensitivity of the inversion
6.4. Results.

![Graph of exchange-correlation potentials](image)

Figure 6.4: Exchange-correlation potentials $v_{xc}(r)$ (upper part) and $r \times v_{xc}(r)$ (lower part) for He and Be as obtained in this work and in Refs. [276], [290]; full line: He (this work), dashed line: He (high-level calculation [276]); dotted line: Be (this work), dot-dashed line: Be (QMC [290]).

The algorithm of section 6.2 is applied to a number of light atoms: the closed-
shell systems He, Be, Ne, Mg, and Ar along with the open-shell atoms B, C, N, O, and F. We reached fast convergence [according to the criterion Eq. (6.8)] for each atom in our study. This means that we have found a basis-set free representation of the KS xc potential, and that we obtained the unique potential corresponding to our Dyson(2) input densities, up to some arbitrary constant. Note that it is not guaranteed that the scheme will converge for an arbitrary input density, since in principle there may be densities that are not noninteracting \( \psi \)-representable [258].

At convergence, we not only reproduce the input density in an accurate way, but also the highest occupied KS eigenvalue coincides with the Dyson(2) ionization energy (with an accuracy of about \( 10^{-7} \) a.u. or better). Moreover, the potentials show the correct asymptotic behavior \( \sim -\frac{1}{r} \). This feature is not imposed on the potential by hand, but is generated automatically, probably due to the feedback mechanism between the update of the potential, the KS orbitals, and the physical input density having the correct large-\( r \) behavior of Eq. (6.9). To explain this in more detail, let us consider an electron of a neutral atom at a very large distance from the nucleus. As is well-known, the electron experiences a nuclear potential,
6.4 Results.

![Graphs showing potentials](image)

Figure 6.6: Potentials of present work for Mg (full line) and Ar (dashed) [$v_{xc}(r)$ (upper part) and $r \times v_{xc}(r)$ (lower part)]

shielded by the other $(Z-1)$ electrons. The influence of the nucleus on the electron is then expressed by $-\frac{Z}{r}$. The nuclear potential $-\frac{Z}{r}$ and the Hartree field $v_J(r) = \int d^3r' \frac{\rho(r')}{|r-r'|}$, however, cancel each other at large distances, such that the residual $-\frac{1}{r}$ potential must be generated by the xc potential.

In Figs. 6.4, 6.5, and 6.6, we group the xc potentials from our scheme for the closed-shell systems. The upper part shows the potential itself, while the lower part involves $r \times v_{xc}(r)$ in order to illustrate in a more transparent way the correct asymptotic behavior of the potential.

For comparison, we also include a high-level xc potential for He obtained by Umrigar and Gonze [276], as well as quantum-Monte-Carlo (QMC) results for Be and Ne obtained by the same authors [275] and by Filippi, Umrigar, and Gonze [273]. These high-level potentials have also been used in Refs. [164], [165], and [291]. It is clear that our results agree very well with these potentials, especially in the case of helium. In the last case, our potential only differs from the high-level potential at the origin [in the lower part of Fig. 6.4, with $r \times v_{xc}(r)$, the two curves practically coincide].
Figure 6.7: Exchange-correlation potentials $v_{xc}(r)$ (upper part) and $r \times v_{xc}(r)$ (lower part) of present work for B: majority spin in full line, minority spin in dashed line.

The spin-up and spin-down potentials for the open-shell B, C, N, O, and F atoms are displayed in Figs. 6.7-6.10. Note that the spin-up and spin-down potentials for F (Fig. 6.10) are very alike, as the atom approaches a closed-shell configuration.

The lower part of each figure displaying $r \times v_{xc}(r)$ systematically reveals the correct asymptotic behavior of the xc potential. Also, we find that the xc potential has a finite value at the origin, as was already suggested by Morrison et al. [292]. This was also mentioned as one of the properties of the exact xc potential in section 5.6. The $r \times v_{xc}(r)$ curves provide a very sensitive look at the long-range behavior of the xc potentials. Comparing, for the case of Ne in Fig. 6.5, the result of this work with the QMC result, it is clear that two spurious extrema appear in the potential based on the Dyson(2) density. Such artificial structure is present for the xc potentials of the other atoms as well, and is related to the extrapolation procedure in the asymptotic region of the density. Though we take care to extrapolate in a smooth manner, the procedure still affects (mildly) the xc potential near the extrapolation point. The effect is entirely due to imperfections in the extrapolated Dyson(2) input density, and not to the used inversion procedure, since we do not encounter it when we use HF input densities or the QMC neon density, which was communicated to us by
Figure 6.8: Exchange-correlation potentials \( v_{xc}(r) \) (upper part) and \( r \times v_{xc}(r) \) (lower part) of present work for N: majority spin in full line, minority spin in dashed line.

Gonze [290]. This observation is similar to the appearance of spurious oscillations in the xc potential reported by Schipper et al. [269] when a Gaussian-type input density is used. Here we impose on the input density the correct asymptotic behavior by extrapolation, leading to less pronounced and more localized oscillations near the extrapolation point.

A characteristic feature, present in all figures, is the appearance of the intershell peaks. They can be partly explained by the jump of the exchange-hole from one shell to another if the reference position crosses the border region between the two shells (see Refs. [293]-[295]).

Since the xc potential constructed with the presented algorithm results in an almost perfect reproduction of the input density, one may assume that all correlations involved in the density are also present in the xc potential. Therefore the xc potentials obtained in the present study incorporate all Dyson(2) correlations, i.e. all correlations of the self-consistent Green’s function scheme up to second-order in the Coulomb interaction.
Figure 6.9: Exchange-correlation potentials $v_{xc}(r)$ (upper part) and $r \times v_{xc}(r)$ (lower part) of present work for O: majority spin in full line, minority spin in dashed line.

6.5 Applications of the exact xc potentials.

The generated xc potentials can be used in a variety of applications. In this work, we focussed on two examples: the calculation of the kinetic contribution to the xc energy (subsection 6.5.1) and use of the potentials in a (re)fitting procedure of an existing xc functional (subsection 6.5.2). The latter application is somewhat related to the work performed in the mid-1980s when researchers tried to assess the quality of the first examples of the GGA class functionals (see e.g. [280]). In the present work, we perform a preliminary study on one of the most advanced GGA functionals, namely the HCTH functional (see also section 5.5.4).

6.5.1 Constituent parts of the xc energy.

First of all, let us study the xc energy and its components (the exchange-only energy and the correlation energy):

$$
E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (W[\rho] - J[\rho])
= T_c[\rho] + (W[\rho] - J[\rho]).
$$

(6.20)
To calculate $E_{xc}[\rho]$, we derive from expression (5.58) that

$$E_{xc}[\rho] = E_{gs} - \sum_{i(\text{occ.})} \epsilon_i^{KS} + J[\rho] + 4\pi \sum_\sigma \int d^3r \, r^2 \, \psi_{\text{imp}}(r)_\sigma \rho_\sigma(r), \tag{6.21}$$

in which $E_{gs}$ can be approximated by the Dyson(2) ground-state energy $E_{0[A]}$ of the many-electron system $A$, while for the KS eigenvalues $\epsilon_i^{KS}$ those can be taken as generated by the inversion scheme.

The exchange-only part $E_x[\rho]$ is calculated with the Fock expression for exact exchange, but using the KS orbitals instead of the HF orbitals [see also Eq. (5.111) and Ref. [144]]:

$$E_x[\rho] = \langle \Phi_0 | \hat{W} | \Phi_0 \rangle - \frac{1}{2} \int d^3r_1 \int d^3r_2 \, \frac{\rho(r_1) \rho(r_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$= -\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \delta_{m_i, m_j} \int d^3r_1 \int d^3r_2 \, \frac{\phi_i^{KS}(r_1) \phi_j^{KS}(r_2) \phi_i^{KS}(r_1) \phi_j^{KS}(r_2)}{|\mathbf{r}_1 - \mathbf{r}_2|},$$

Figure 6.10: Exchange-correlation potentials $\nu_{xc}(r)$ (upper part) and $r \times \nu_{xc}(r)$ (lower part) for F; inversion scheme: majority spin of F (full), minority spin of F (dashed); HCTH functional with new exchange parameters: majority spin of F (dotted), and minority spin of F (dot-dashed).
where $|\Phi_0\rangle$ again denotes the Slater determinant formed by the $N$ lowest KS orbitals.

Table 6.1: Estimates of xc energy along with the exchange-only part $E_{xc}[\rho]$ and the kinetic contribution $T_c[\rho]$ to the correlation energy. First two numerical columns represent the total xc energy according to Eq. (6.21) and the exchange-only energy as calculated from taken from Eq. (6.22). The third column represents the total correlation energy $E_c[\rho] = E_{xc}[\rho] - E_{x}[\rho]$. Fourth, fifth, and sixth column are predictions for $T_c[\rho]$. Values of Whittingham and Burke (WB) are obtained from Ref. [296], values of Morrison and Zhao (MZ) are taken from [292].

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<th>$E_{xc}[\rho]$</th>
<th>$E_x[\rho]$</th>
<th>$E_c[\rho]$</th>
<th>$T_c[\rho]$ (WB)</th>
<th>$T_c[\rho]$ (MZ)</th>
<th>$T_c[\rho]$ [Dyson(2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
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<td>-1.0229</td>
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<td>0.038</td>
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<tr>
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<td>-0.1413</td>
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<td>0.15</td>
<td>0.139</td>
</tr>
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</tr>
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<td>0.355</td>
</tr>
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<td>0.372</td>
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<tr>
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<td>-15.9611</td>
<td>-0.3353</td>
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<td>Al</td>
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<td>0.369</td>
<td>0.35</td>
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</tr>
<tr>
<td>Si</td>
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<td>0.392</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td>0.429</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td>0.476</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td></td>
<td></td>
<td>0.532</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>-30.7461</td>
<td>-30.1437</td>
<td>-0.6024</td>
<td>0.589</td>
<td>0.21</td>
<td>0.563</td>
</tr>
</tbody>
</table>

In Table 6.1, we collect the predictions for the xc energy $E_{xc}[\rho]$, exchange-only energy $E_x[\rho]$, total correlation energy $E_c[\rho]$, and the kinetic contribution $T_c[\rho]$ to the xc energy. It is clear that the exchange part dominates by far all quantum-mechanical effects incorporated in the xc potential. Note that the values for exact exchange represented here with the KS orbitals are very similar to the exact-exchange results in Ref. [203], where the Fock expression was used with the HF orbitals (in this reference a discussion can be found as well on the accuracy of some GGA functionals in describing correlations). This supports the statement made at the end of section 5.4.2 that the KS orbitals are quite similar to the HF orbitals. Nevertheless, although
the exchange part dominates, the correlation influence is crucial for an accurate description of a many-electron system by means of DFT.

To evaluate the kinetic energy contribution $T_c[\rho]$ to the correlation energy, the virial theorem can be used: $T_c[\rho] = T[\rho] - T_s[\rho] = -E[\rho] - T_0[\rho]$, where $E[\rho]$ is the exact total ground-state energy of the interacting system. We approximated this total energy by means of the Dyson(2) energy $E_{0(\lambda)}$ of Tables 3.10 and 4.6. It is clear from the table that $T_c[\rho]$ is smaller than the two-body repulsion contribution $E_{\text{ee}}[\rho] = W[\rho] - J[\rho] - E_2[\rho]$ to the total correlation energy $E_c[\rho] = E_{xc}[\rho] - E_2[\rho]$. We see that roughly (cf. [264])

$$T_c[\rho] \approx -\frac{1}{2} E_{\text{ee}}[\rho] \approx -E_c[\rho].$$  \hspace{1cm} (6.23)

We also observe that the kinetic contribution $T_c[\rho]$ is always positive as was argued in chapter 5. Because $T_c[\rho]$ is calculated as the difference of two large quantities, the accuracy of its prediction is not that high. We report results for $T_c[\rho]$ obtained by other methods as well ([296],[292]) and note that the predictions may vary between the schemes. However, from the table we see that the Dyson(2) results tend to favor the predictions made by Whittingham and Burke. Especially the value for argon predicted by Morrison and Zhao appears to be too small, although the method of these authors seems valuable for lighter elements.

As a second example, we consider the use of the generated xc potentials in a fitting procedure for an existing functional parametrization. The resulting parameter set can then be considered to be derived on a fully microscopic basis, i.e. without fitting to experimental data. This will be illustrated in the next subsection with some preliminary results.

### 6.5.2 Use of the potentials in fitting procedures.

As mentioned in the introduction to this chapter, the asymptotic region of the xc potential becomes more and more prerequisite in present-day applications of DFT. In this respect, there are actually two problems with current popular xc functionals, as was addressed in section 5.5.5: the asymptotic $-\frac{1}{r}$ behavior of the xc potential and the derivative discontinuity. It was explained that to remove the ambiguity in the constant appearing in the xc potential at integer number of electrons, we can define the xc potential as an average of the electron-deficient and the electron-abundant side.

It was observed by Tozer and Handy [249, 252] that Generalized Gradient Approximation (GGA) functionals could more easily be fitted to exact xc potentials if they left room for a system-dependent constant in the fit. They interpreted this as an indication that the GGA potentials represent an average of the electron-deficient and the electron-abundant limit of the exact xc potential. The same method was used by Hamprecht et al. [247], who fitted their model xc potential to both energetic
data and accurate xc potentials obtained in the ZMP scheme. Note that these ZMP potentials have the correct asymptotic behavior, just as in our scheme. Including exact xc potentials provides more detailed information on how the model potential should behave, which may result in improved asymptotic densities and more accurate optimized geometries. It should be noted that good structural predictions can also be obtained by including exact exchange in the functional, and fitting to energetic data solely.

To include the derivative discontinuity to some extent in the functional, Hamprecht et al. allowed for a system-dependent constant shift of the input potentials. This shift does not enter the parameters of the functional explicitly, but has an indirect effect on the value of the parameters. Yet, the expansion defining the so-called HCTH functional leads to a potential that does not go to a constant but vanishes asymptotically [see Eqs. (5.117) and (5.118)]. Further improvements to the functional were implemented by Tozer and Handy [249], who asymptotically corrected the HCTH potential. Their approach implies, however, that the corrected potential cannot be written easily as the derivative of an xc functional.

Table 6.2: Parameters of the HCTH functional: the first numerical column collects the original values obtained by Hamprecht et al., the next columns present the sets obtained using the Dyson(2) energies and xc potentials in the fit for different weights \( w_A \) of the energetic part of the objective function. Parameters are displayed which are obtained when varying only the exchange (x) parameters as well as varying both the exchange and the first three orders in correlation (x+c).

<table>
<thead>
<tr>
<th>Coeff.</th>
<th>Ref. [247]</th>
<th>exchange only ( w_A = 10 )</th>
<th>exchange only ( w_A = 100 )</th>
<th>exchange only ( w_A = 1000 )</th>
<th>( x + c ) ( w_A = 10 )</th>
<th>( x + c ) ( w_A = 100 )</th>
<th>( x + c ) ( w_A = 1000 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( c_1 )</td>
<td>1.09330</td>
<td>1.089</td>
<td>1.089</td>
<td>1.078</td>
<td>1.091</td>
<td>1.059</td>
<td>1.051</td>
</tr>
<tr>
<td>( c_2 )</td>
<td>0.222601</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.921</td>
<td>1.231</td>
<td>2.164</td>
</tr>
<tr>
<td>( c_3 )</td>
<td>0.729974</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-1.513</td>
<td>0.6931</td>
<td>1.029</td>
</tr>
<tr>
<td>( c_4 )</td>
<td>-0.744056</td>
<td>-0.9258</td>
<td>-0.9038</td>
<td>-0.8424</td>
<td>-0.6457</td>
<td>-0.4957</td>
<td>-0.6129</td>
</tr>
<tr>
<td>( c_5 )</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.6577</td>
<td>-0.3981</td>
<td>-0.4234</td>
</tr>
<tr>
<td>( c_6 )</td>
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<td>-</td>
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<td>-2.679</td>
<td>-3.602</td>
</tr>
<tr>
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<td>8.599</td>
<td>7.414</td>
<td>6.818</td>
<td>6.719</td>
</tr>
<tr>
<td>( c_8 )</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>( c_9 )</td>
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<td>-</td>
<td>-</td>
<td>-11.90</td>
<td>-11.258</td>
<td>-10.03</td>
</tr>
<tr>
<td>( c_{11} )</td>
<td>-0.802496</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( c_{12} )</td>
<td>8.08564</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
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<td>( c_{13} )</td>
<td>4.49357</td>
<td>7.168</td>
<td>8.443</td>
<td>17.42</td>
<td>7.746</td>
<td>7.119</td>
<td>8.869</td>
</tr>
<tr>
<td>( c_{14} )</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( c_{15} )</td>
<td>-4.47857</td>
<td>-</td>
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</tr>
</tbody>
</table>
6.5. Applications of the exact xc potentials.

In order to illustrate the use of the xc potentials resulting from our Dyson(2) calculations, we have made a refit of the HCTH functional. We selected this functional because it has been designed with the correct asymptotic behavior in mind. Currently, our training set only consists of the closed- and open-shell systems in our study, and results are therefore preliminary.

The HCTH xc functional can be written as

$$E_{xc}[\rho] = \sum_i c_i \int f_i(\rho_\uparrow, \zeta_\uparrow, \rho_\downarrow, \zeta_\downarrow) d^3r,$$

(6.24)

where \(\rho_\sigma\) is the one-body spin density, \(\zeta_\sigma = |\nabla \rho_\sigma|\), and the expansion functions \(f_i\) are described in section 5.5.4 [Eqs. (5.117) and (5.118)]. In the HCTH functional, 15 functions \(f_i\) have been considered. The 15 expansion coefficients \(c_i\) are optimized in a least-squares fit with an objective function \(\Omega\) that consists of two parts \(\Omega = \Omega_V + \Omega_E\). The first part \(\Omega_V\) involves the potentials

$$\Omega_V = \sum_\sigma \sum_A^{\text{atom}s} 4\pi \int dr \ r^2 \left[ v_{\text{inpul}}^{A\sigma}(r) + k_A^\sigma - \sum_i c_i v_i^{A\sigma}(r) \right]^2 \rho_{A\sigma}^{2/3}(r),$$

(6.25)

where \(v_{\text{inpul}}^{A\sigma}(r)\) is the xc potential for atom \(A\) as derived using our inversion algorithm, \(k_A^\sigma\) is the constant shift allowed for this potential, \(v_i^{A\sigma}(r)\) is the potential derived from the function \(f_i^{A\sigma}(r)\) by functional derivation with respect to \(\rho_{A\sigma}(r)\), and \(\rho_{A\sigma}^{2/3}(r)\) is an appropriate weighting factor. This weighting factor was also used by Hamprecht et al. in the original fitting procedure of the HCTH functional.

The second term \(\Omega_E\) in the objective function involves the energetic data,

$$\Omega_E = \sum_A^{\text{atom}s} w_A \left[ E_{xc}^A - 4\pi \sum_i c_i \int f_i^A(r) r^2 \ dr \right]^2.$$

(6.26)

The xc energies \(E_{xc}^A\) were determined by means of expression (6.21) [where, of course, the direct Coulomb interaction \(J[\rho]\) is evaluated with the total density \(\rho(\vec{r}) = \rho_A(\vec{r}) + \rho_{A\uparrow}(\vec{r}) + \rho_{A\downarrow}(\vec{r})\)]. The weights \(w_A\) in Eq. (6.26) balance the influence of the potential and energetic part in the fit.

In the original derivation of the HCTH functional [247], Hamprecht et al. introduced a self-consistent technique to determine the value of the system-dependent shifts \(k_A^\sigma\) (see also Ref. [252]). In the present study, we found no need for this procedure, but simply minimized the objective function with respect to both the functional parameters \(\{c_i\}\) and the constant shifts \(\{k_A^\sigma\}\). The conditions

$$\frac{\partial \Omega}{\partial c_i} = 0; \quad \frac{\partial \Omega}{\partial k_A^\sigma} = 0,$$

(6.27)
with $\Omega = \Omega_V + \Omega_E$ then lead to the least-squares equations

$$
\begin{align*}
c_i : \quad & \sum_{j=1}^{N_p} A_{ij} \ c_j + \sum_{\sigma'} \sum_{M=1}^{N_s} A_{iM,\sigma'} \ k_M^{\sigma'} = B_i, \quad i = 1, \ldots, N_p; \\
k_A^\sigma : \quad & \sum_{j=1}^{N_p} A_{A,\sigma j} \ c_j + \sum_{\sigma'} \sum_{M=1}^{N_s} A_{A M,\sigma} \ k_M^{\sigma'} = B_{A \sigma}, \quad A = 1, \ldots, N_A,
\end{align*}
$$

(6.28)

where $N_p$ and $N_A$ are the numbers of parameters and atoms respectively. The matrices $A$ and $B$ are given by

$$
\begin{align*}
A_{ij} &= \sum_{\sigma'} \sum_{N=1}^{N_s} \left[ dr \ r^2 \ v_i^{N\sigma'}(r) \ v_j^{N\sigma'}(r) \ \rho_{N\sigma'}^2(r) \right] + 4 \pi \ \omega_N \ \int dr \ r^2 \ f_i^N(r) \ \int dr \ r^2 \ f_j^N(r) \\
A_{iM,\sigma'} &= - \int dr \ r^2 \ v_i^{M\sigma'}(r) \ \rho_{M\sigma'}^2(r) \\
B_i &= \sum_{\sigma'} \sum_{N=1}^{N_s} \left\{ \int dr \ r^2 \ v_i^{N\sigma'}(r) \ v_i^{N\sigma'}(r) \ \rho_{N\sigma'}^2(r) + \omega_N \ E_{xc}[\rho_N] \ \int dr \ r^2 \ f_i^N(r) \right\}
\end{align*}
$$

(6.29)

for $c_i$ and

$$
\begin{align*}
A_{A,\sigma j} &= - \int dr \ r^2 \ \rho_{A\sigma}^2(r) \ v_j^{A\sigma}(r) \\
A_{A, M, \sigma'} &= \delta_{AM} \delta_{\sigma\sigma'} \ \int dr \ r^2 \ \rho_{A\sigma}^2(r) \\
B_{A \sigma} &= - \int dr \ r^2 \ \rho_{A\sigma}^2(r) \ v_{A\sigma}^{impul}(r)
\end{align*}
$$

(6.30)

for $k_A^\sigma$.

In this preliminary fit we have substantially less fitting data (potentials and total energies of only ten atoms) than in the original parametrization by Hamprecht et al. [247], which involved basically the G2 training set. As a result, some coefficients $c_i$ tend to oscillate when allowed to vary freely in the fit. Therefore, we fixed the coefficients corresponding to the correlation terms in the expansion and applied the least-squares fit on the exchange parameters only (i.e. the coefficients $c_1$, $c_4$, $c_7$, $c_{10}$, and $c_{13}$) along with the system-dependent shifts $k_A^\sigma$.

In Table 6.2, we collect the original values of the parameters [247] together with our values for a few choices of the weights $\omega_A$. For simplicity, the weight is kept the same for all atoms. We also include the parameters obtained when allowing the exchange and the first three correlations orders to vary. We see that some parameters tend to differ substantially from the original parametrization, which we attribute to the reduced size of our training set. In the remainder of this chapter, we will therefore report only results that are obtained with the parameter set in which
Table 6.3: Total energy for the closed-shell systems as predicted by the HCTH functional fitted to Dyson(2) quantities, for different values of the weight \( w_A \) in the fit. The last two rows respectively represent the total energies of the Dyson(2) scheme and the HCTH functional using the original parameters [247]. Also listed are results for Ca, which was not included in the training set. For Ca the Dyson(2) prediction is not available, and the energy denoted as ‘Dyson(2)’ is taken from a G3 calculation [297]. All results are in atomic units.

<table>
<thead>
<tr>
<th>( w_A )</th>
<th>He</th>
<th>Be</th>
<th>Ne</th>
<th>Mg</th>
<th>Ar</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-2.918</td>
<td>-14.662</td>
<td>-128.875</td>
<td>-199.973</td>
<td>-527.430</td>
<td>-677.468</td>
</tr>
<tr>
<td>100</td>
<td>-2.913</td>
<td>-14.651</td>
<td>-128.870</td>
<td>-199.970</td>
<td>-527.436</td>
<td>-677.480</td>
</tr>
<tr>
<td>Dyson(2)</td>
<td>-2.899</td>
<td>-14.628</td>
<td>-128.888</td>
<td>-199.948</td>
<td>-527.422</td>
<td>-677.38450</td>
</tr>
<tr>
<td>HCTH</td>
<td>-2.918</td>
<td>-14.670</td>
<td>-128.962</td>
<td>-200.096</td>
<td>-527.678</td>
<td>-677.765</td>
</tr>
</tbody>
</table>

merely the exchange parameters were optimized, while the correlation parameters were fixed on the original HCTH value.

The total energies as predicted using the HCTH functional (with the new exchange parameters of Table 6.2) for the atoms of the training set and also for calcium are listed in Tables 6.3 and 6.4. All results were obtained by solving the KS equations in coordinate space. The Dyson(2) energies used in the fitting procedure are given for comparison, as well as the outcome of a G3 calculation for calcium [297]. Note that this G3 calculation involves relativistic corrections, which can have a relatively important influence in an atom as calcium. These corrections were not included in our Dyson(2) study. The results using the original parametrization of the HCTH functional are listed as well. Mind, however, that the HCTH functional was fitted to experimental energies (amongst other quantities) and not to \textit{ab initio} energies as in the present study.

In Tables 6.5 and 6.6 the first ionization energies are presented along with the Dyson(2) ionization energies, and the constant shifts \( k_A \) of the atoms in our training set. In Table 6.6, only the shift of the potential that corresponds to the spin which determines the first-ionization level is reported. The shift of the potential corresponding to the other spin polarization is of a similar value. The ionization energy is calculated according to [247]

\[
\mathcal{I}_A = -\frac{E_{\text{ion}}^{KS}}{K_A} + k_A. \tag{6.31}
\]

Note that the ionization energies were not included in the fit. Nevertheless, we notice a good agreement with the Dyson(2) quantities. We observe that all shifts are positive and of the expected order of magnitude: theoretical considerations (see
Table 6.4: Total energy for the open-shell systems as predicted by the HCTH functional fitted to Dyson(2) quantities, for different values of the weight $w_A$ in the fit. See also caption of Table 6.3.

<table>
<thead>
<tr>
<th>$w_A$</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>-24.619</td>
<td>-37.801</td>
<td>-54.545</td>
<td>-75.003</td>
<td>-99.662</td>
</tr>
<tr>
<td>1000</td>
<td>-24.612</td>
<td>-37.797</td>
<td>-54.539</td>
<td>-75.006</td>
<td>-99.671</td>
</tr>
<tr>
<td>Dyson(2)</td>
<td>-24.600</td>
<td>-37.789</td>
<td>-54.543</td>
<td>-75.010</td>
<td>-99.678</td>
</tr>
<tr>
<td>HCTH</td>
<td>-24.645</td>
<td>-37.837</td>
<td>-54.593</td>
<td>-75.063</td>
<td>-99.737</td>
</tr>
</tbody>
</table>

section 5.5.5) indicate that this shift should be less than or equal to the hardness $\frac{\Delta E}{\Delta N}$, where $\Delta N$ is the electron affinity. Similar values of the shifts were obtained in [298] and [299] using other functionals.

In Tables 6.5 and 6.6, we also give the predictions of the hardness in the Dyson(2) scheme. Since the closed-shell systems that were considered cannot bind an extra electron, the hardness equals half the ionization energy. This observation also holds for nitrogen. As was pointed out in section 5.5.5, the constant shift equals the hardness whenever the ground state of the positive and negative ions can be obtained by removing or adding an electron in the same highest occupied KS level of the neutral atom. In the other case, the shift should be less than the hardness. We see that the fitting procedure indeed reveals this trend: the shift of the closed-shell systems is always less than the Dyson(2) hardness, while the shift of the open-shell systems is close to it. Of course, the fitting scheme does not reproduce the open-shell hardness exactly, but it is clear that the predicted shifts oscillate around the exact value. The larger deviation of the nitrogen value may be due to the fact that in this system one 2p spin orbital is assumed fully occupied, while the other one is completely empty. Since in the spin-unrestricted treatment of nitrogen, we do not put the additional electron in the last occupied KS spin orbital of the neutral atom, we can understand that the shift is below the hardness for this atom.

We also note that in Ref. [252] it was argued that a shift which differs significantly from the hardness indicates that kinetic-energy effects give an important contribution to the derivative discontinuity of the xc potential of the corresponding atom.

Apart from a discussion of the energetic predictions of the HCTH functional with the new exchange parameters, we can also compare the HCTH potential with the ones derived in the inversion scheme. This is illustrated for fluor in Fig. 6.10. For the new exchange parameters, we chose those in Table 6.2 corresponding to the weight $w_A = 100$. The HCTH potential has the correct qualitative behavior in the
Table 6.5: Upper part: closed-shell first-ionization energies $I$ obtained with the HCTH functional, for the three sets of parameters corresponding to the weights $w_A = 10, 100, 1000$ in Table 6.2, and the Dyson(2) ionization energy. Lower part: the constant shifts $k_A$ of the potentials as determined by the fit, and the Dyson(2) value for the hardness. All results are in atomic units.

<table>
<thead>
<tr>
<th>$w_A$</th>
<th>He</th>
<th>Be</th>
<th>Ne</th>
<th>Mg</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I$</td>
<td></td>
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<tr>
<td>10</td>
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<td>0.347</td>
<td>0.763</td>
<td>0.243</td>
<td>0.561</td>
</tr>
<tr>
<td>100</td>
<td>0.900</td>
<td>0.347</td>
<td>0.764</td>
<td>0.242</td>
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</tr>
<tr>
<td>1000</td>
<td>0.902</td>
<td>0.346</td>
<td>0.766</td>
<td>0.243</td>
<td>0.563</td>
</tr>
<tr>
<td>Dyson(2)</td>
<td>0.906</td>
<td>0.320</td>
<td>0.763</td>
<td>0.274</td>
<td>0.585</td>
</tr>
<tr>
<td></td>
<td>$k_A$</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>0.144</td>
<td>0.274</td>
<td>0.075</td>
<td>0.184</td>
</tr>
<tr>
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<td>0.272</td>
<td>0.073</td>
<td>0.183</td>
</tr>
<tr>
<td>1000</td>
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<td>0.142</td>
<td>0.276</td>
<td>0.072</td>
<td>0.187</td>
</tr>
<tr>
<td>hardness</td>
<td>0.453</td>
<td>0.160</td>
<td>0.381</td>
<td>0.137</td>
<td>0.293</td>
</tr>
</tbody>
</table>

region where the atomic density is substantial, but it breaks down in the asymptotic regime. As mentioned before, the behavior of the HCTH potential at infinity can be corrected [249].

### 6.6 Generalization of the Kohn-Sham scheme.

Apart from a study of the components of the xc energy and a refit of present-day functionals, the Green’s function calculations can also be used to establish a generalized version of the Kohn-Sham (KS) scheme. In this section, we will describe the preliminary concept of this generalization. Recently there has been some interest in ways to generalize the KS equations. First attempts tried to include a non-local potential in the equations (Refs. [300], [301]). In this section, we will focus on the extension in which we try to model the xc potential based on concepts from Green’s function theory, such as the electron self-energy. The modeling of a universal xc potential may be less troublesome along these lines. Work in the same field of interest can be found in Ref. [302].

As was discussed in chapters 3 and 4, the Green’s function of the atomic system was described, during the successive iterations towards self-consistency, using 20 to 25 BAGEL poles. It was explained that the BAGEL scheme involving $M$ poles reproduces the first $2M+2$ order moments of the (total) Green’s function. However, in the Galitskii-Migdal formula [see Eqs. (3.98) and (4.23)] for the total energy, only
Table 6.6: Upper part: open-shell first-ionization energies $I$ obtained with the HCTH functional and Dyson(2) ionization energy. Lower part: the constant shifts $k_A^e$ and Dyson(2) hardness. Only the shift of the potential that determines the ionization level is considered; the shift of the potential corresponding to the other spin polarization is about the same value. All results are in atomic units.

<table>
<thead>
<tr>
<th>$w_A$</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.302</td>
<td>0.409</td>
<td>0.529</td>
<td>0.494</td>
<td>0.619</td>
</tr>
<tr>
<td>100</td>
<td>0.302</td>
<td>0.409</td>
<td>0.529</td>
<td>0.495</td>
<td>0.620</td>
</tr>
<tr>
<td>1000</td>
<td>0.303</td>
<td>0.409</td>
<td>0.527</td>
<td>0.502</td>
<td>0.623</td>
</tr>
<tr>
<td>Dyson(2)</td>
<td>0.305</td>
<td>0.415</td>
<td>0.537</td>
<td>0.484</td>
<td>0.619</td>
</tr>
<tr>
<td></td>
<td>$k_A^e$</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.162</td>
<td>0.190</td>
<td>0.226</td>
<td>0.246</td>
<td>0.253</td>
</tr>
<tr>
<td>100</td>
<td>0.160</td>
<td>0.189</td>
<td>0.225</td>
<td>0.244</td>
<td>0.251</td>
</tr>
<tr>
<td>1000</td>
<td>0.159</td>
<td>0.190</td>
<td>0.227</td>
<td>0.242</td>
<td>0.252</td>
</tr>
<tr>
<td>hardness</td>
<td>0.149</td>
<td>0.185</td>
<td>0.268</td>
<td>0.226</td>
<td>0.246</td>
</tr>
</tbody>
</table>

the moments of zeroth and first order of the backward distribution of the Green's function are required:

$$E_{gs} = \frac{1}{2} Tr \left\{ (\hat{T} + \hat{V}) \hat{M}^b(0) + \hat{M}^b(1) \right\}. \quad (6.32)$$

In this expression, $Tr$ stands for the trace operator acting on operators in single-particle (s.p.) space, $\hat{T}$ is the kinetic-energy operator and $\hat{V}$ is the one-body operator corresponding to the external field. Furthermore, $\hat{M}^b(k)$ is the operator corresponding to the backward moment of order $k$ of the Green’s function. In the basis that we have used [see e.g. Eq. (3.20)], the matrix representation of the moments is assumed to be diagonal and reads

$$M^b_a(k) = \sum_j S^b_{aj} (\epsilon^b_{aj})^k, \quad (6.33)$$

where $S^b_{aj}$ is the spectroscopic strength of BAGEL pole $j$ of the backward part of the Green's function describing orbital $a$ and $\epsilon^b_{aj}$ is the corresponding pole. The forward moment is defined analogously, by employing the forward instead of the backward quantities. We also recall that the moment of order $k$ of the total Green’s function distribution is defined as [see Eq. (3.91)]

$$M_a(k) = M^b_a(k) + M^f_a(k) = \sum_j S_{aj} (\epsilon_{aj})^k, \quad (6.34)$$
where the sum now runs over all poles, of both the backward as well as the forward part.

As the first two energy-weighted moments are sufficient in Eq. (6.32), it is plausible that a three-pole representation of the Green’s function should already give high enough an accuracy for the total energy, as borne out by nuclear-matter calculations (see [106] and [303]). These calculations also indicate that three poles provide a good description of the quasi-particle properties. In a three-pole scheme, one pole will contain the quasi-particle excitations (which are more sensitive to the effects of the external field), while the other two poles will account for the universal background of the Coulomb interaction between the electrons. For Green’s functions describing a hole orbital, we use two poles in the backward part of the spectrum [quasi-particle spectroscopic strength $S^b_a$ and energy $\epsilon^b_a$ along with an additional backward pole $\epsilon^b_a$ with strength $S^b_a$] and one pole in the forward part (s.p. energy $\epsilon^f_a$ with strength $S^f_a$). For Green’s functions describing a particle orbital, we take one pole in the backward and two poles in the forward part. Summarizing, we have that $(S^b_a, \epsilon^b_a)$ will collect the main quasi-particle contributions, while $(S^f_a, \epsilon^f_a)$ will describe the universal background of the two-body interaction, i.e. the correlation effects that are present in any system governed by the Coulomb interaction.

The goal of this three-pole treatment of the Green’s function is to derive quasi-particle equations that are similar to the KS equations and provide us with a means to study an interacting many-body system using s.p. equations. The total self-energy can be divided in a natural way into a static (energy-independent) part and a dynamic part (this is common practice in the study of energy-dependent quantities, such as the polarizability of solids, and is valid for systems with a well-behaved two-body interaction)

$$\Sigma(E) = \Sigma_{\text{static}} + \Delta \Sigma(E), \quad (6.35)$$

where

$$\lim_{E \to \infty} \Delta \Sigma(E) = 0. \quad (6.36)$$

This decomposition is illustrated in Fig. 6.11, which can be compared with Fig. 2.10. Note that the static part of the self-energy $\Sigma_{\text{static}}$ has the same structure as the Hartree-Fock mean field $\tilde{V}_{HF}$, but must be evaluated with the Green’s function of the system described by the full self-energy $\Sigma_{\text{static}} + \Delta \Sigma(E)$. This was also the case in the Dyson(2) scheme, where we renormalized the Hartree-Fock energies by using the second-order Green’s function in the evaluation [see Eqs. (3.30) and (4.22)]. To emphasize this, we denote the static part of the self-energy by $\Sigma_{\text{static}} = \tilde{V}_{HF}[\rho]$, which means that the Hartree-Fock field must be evaluated with the one-body density (matrix) of the interacting system.

To keep this discussion as general as possible, we will not use a basis representation of the Green’s function, but retain the operator notation for the time being.
The operator representation of Dyson’s equation in the form of Eq. (2.42) is

$$\hat{G}(E) = \frac{1}{\hat{G}^{(0)}(E) - \hat{\Sigma}(E)} = \int dE' \frac{\hat{S}(E')}{E - E'}.$$  \hspace{1cm} (6.37)

The last equation is a generalization of Lehmann’s representation (2.18) and defines the spectral operator $\hat{S}(E)$. It is clear (see also Ref. [107]) that $\hat{S}(E)$ is the operator corresponding to the spectral functions (2.20) and (2.21). Note that in this discussion, we will not include the infinitesimal convergence parameter $\eta$ which implies that $\hat{S}(E)$ describes both the forward and backward part of the Green's function. In a finite system, the operator $\hat{S}(E)$ will involve a sum over $\delta$-distributions corresponding to the bound states in the $A \pm 1$ system. This turns the continuous integration over the negative part of the energy spectrum in Eq. (6.37) into a discrete sum as in the Lehmann representation (2.18). Of course, the continuous part of the spectrum (the branch cuts in Fig. 2.2) will still involve a continuous integration even in case of a finite system. Note that in the previous chapter, we introduced a truncated s.p. basis, in which the continuum is approximated by a sequence of $\delta$-peaks. This means that in our model no continuous part was present.

Using $\hat{S}(E)$, the operator corresponding to the energy-weighted moment of order $k$ can be expressed as:

$$\hat{M}(k) = \int dE' (E')^k \hat{S}(E').$$  \hspace{1cm} (6.38)

As explained in chapter 2, there are various possible choices for the operator $\hat{G}^{(0)}(E)$ in Eq. (6.37). Of course, we must take care of the fact that many-body diagrams which are put into $\hat{G}^{(0)}(E)$ are not included in $\hat{\Sigma}(E)$ [see also Eq. (2.48)]. An appropriate choice here is to include the external field in $\hat{G}^{(0)}(E)$ and to incorporate...
the two-body effects in \( \hat{\Sigma}(E) \). It is clear from Eq. (2.16) that the operator \( \hat{G}^{(0)}(E) \) for this noninteracting system can be written as

\[
\hat{G}^{(0)}(E)^{-1} = E \hat{1} - \hat{T} - \hat{V},
\]

(6.39)

where \( \hat{1} \) is the unity operator. Substituting Eqs. (6.35) and (6.39) in Eq. (6.37), we obtain with \( \hat{\Sigma}_{\text{static}} = \hat{V}_{HF}[\rho] \)

\[
\hat{G}(E) = \frac{1}{E \hat{1} - \hat{T} - \hat{V} - \hat{V}_{HF}[\rho] - \Delta \Sigma(E)} = \int dE' \frac{\hat{S}(E')}{E - E'}.
\]

(6.40)

By expanding the left-hand and right-hand side of this equation in \( 1/E \), we obtain the following relations

\[
\hat{M}(0) = \int dE' \hat{S}(E') = \hat{1}
\]

\[
\hat{M}(1) = \int dE' E' \hat{S}(E') = \hat{T} + \hat{V} + \hat{V}_{HF}[\rho].
\]

(6.41)

Note that the identification \( \hat{M}(1) = \hat{T} + \hat{V} + \hat{V}_{HF}[\rho] \) is consistent with the property \( M(1) = \epsilon_{HF} \) (the Hartree-Fock s.p. energy) derived in section 3.4.4. From Eq. (6.40), we can obtain a clear definition of the concept of the quasi-particle. The denominator \( E \hat{1} - \hat{T} - \hat{V} - \hat{V}_{HF}[\rho] - \text{Re}\{\Delta \Sigma(E)\} - i\text{Im}\{\Delta \Sigma(E)\} \) contains the bulk of the spectroscopic strength at energies for which \( \hat{T} + \hat{V} + \hat{V}_{HF}[\rho] + \text{Re}\{\Delta \Sigma(E)\} - E \hat{1} \) has zero eigenvalue. These eigenstates are known as quasi-particle excitations [304] (see also chapter 2).

We will now determine the generalized KS equations for the quasi-particle states of the interacting many-body system. Therefore, we introduce a basis of vectors \( \{|X_{n}^{\nu}\}; \nu = 1, \ldots, \infty \) which are not necessarily normalized nor orthogonal. The Green’s function of the quasi-particle state can be cast in the form [see also Eq. (2.18)]

\[
\hat{G}^{\nu}(E) = \sum_{\nu=1}^{\infty} \frac{1}{E - \epsilon_{\nu}} |X_{\nu}^{\nu}\rangle\langle X_{\nu}^{\nu}|.
\]

(6.42)

The quasi-particle part of the operator moments of order \( k \) has the following representation in the adopted basis

\[
\hat{M}^{\nu}(k) = \sum_{\nu=1}^{\infty} (\epsilon_{\nu})^{k} |X_{\nu}^{\nu}\rangle\langle X_{\nu}^{\nu}|.
\]

(6.43)

The goal is now to derive an equation for the state \( |X_{\nu}^{\nu}\rangle \) and the corresponding energy \( \epsilon_{\nu}^{\nu} \). Therefore, we consider the following transformation

\[
|\chi_{\mu}^{\nu}\rangle = [\hat{M}^{\nu}(0)]^{-1} |X_{\nu}^{\nu}\rangle,
\]

(6.44)
where we impose the normalization
\[
\langle \chi^q_{\mu} | \hat{M}^q(0) | \chi^q_{\nu} \rangle = \delta_{\mu \nu}.
\] (6.45)

From Eq. (6.43), we find that [note that \( \hat{M}^q(0) \) is a hermitian operator]
\[
\left[ \hat{M}^q(0) \right]^{-1} = \sum_{\nu=1}^{\infty} | \chi^q_{\nu} \rangle \langle \chi^q_{\nu} | \;
\right]
\]
\[
\left[ \hat{M}^q(0) \right]^{-1} \hat{M}^q(1) \left[ \hat{M}^q(0) \right]^{-1} = \sum_{\nu=1}^{\infty} \epsilon_{\nu} | \chi^q_{\nu} \rangle \langle \chi^q_{\nu} | ,
\] (6.46)

which allows to derive the following generalized eigenvalue problem
\[
\hat{M}^q(1) | \chi^q_{\mu} \rangle = \epsilon_{\mu} \hat{M}^q(0) | \chi^q_{\mu} \rangle .
\] (6.47)

The zeroth-order moment \( \hat{M}^q(0) \) acts as a metric operator and takes into account the non-orthogonality of the set \( \{ | \chi^q_{\nu} \rangle \} \). We could apply a Gram-Schmidt orthogonalization [11] or a Löwdin transformation [305] to make the set orthonormal, but the non-orthogonality allows us to work directly with quasi-particle part of the zeroth- and first-order moment in Eq. (6.47), which we prefer.

Eq. (6.43) defines the quasi-particle part of the moment of order \( k \), and if we introduce the notation \( \hat{M}^{bg}(k) \) for the remaining universal background part of the correlations, we have that
\[
\hat{M}^q(0) = \hat{M}(0) - \hat{M}^{bg}(0) \\
= \hat{T} - \hat{M}^{bg}(0) \\
\hat{M}^q(1) = \hat{M}(1) - \hat{M}^{bg}(1) \\
= \hat{T} + \hat{V} + \hat{V}_{HF}[\rho] - \hat{M}^{bg}(1).
\] (6.48)

From these equations we see that if we parametrize the background contribution to the zeroth- and first-order moment, we also have an expression for the quasi-particle part. To find a suitable parametrization, we can employ the results of the second-order Green’s function calculations discussed in chapters 3 and 4. Using the Hartree-Fock basis set introduced in these calculations and adopting the approximation that the Green’s function is diagonal in this basis set, we obtain the following expressions for the moments of order zero and one in the three-pole representation:
\[
M^{bg}_{\alpha}(0) = S^b_{\alpha} + S^f_{\alpha} \\
M^{bg}_{\alpha}(1) = S^b_{\alpha} \epsilon_{\alpha} + S^f_{\alpha} \epsilon_{\alpha}.
\] (6.49)

Based on the ideas of the DFT-KS scheme, we can try to parametrize the moments in terms of the one-electron density. Using this universal parametrization,
we can tackle the quasi-particle equations (6.47), which represent a generalization of the Kohn-Sham scheme: they enable the study of an interacting many-particle system by means of s.p. equations, while allowing for an accurate treatment of the correlation effects present in the Coulomb system. It is easily seen that, due the correlations embedded in the scheme, the occupation numbers \( z^q_{\nu} \) of the quasi-particle orbitals will be bracketed by zero and unity: \( 0 \leq z^q_{\nu} \leq 1 \). Since the orbitals \( | \chi^q_{\nu} \rangle \) are defined as quasi-particle states, they also have a clear physical meaning.

Because the parametrization of the moments \( \tilde{M}^q(0) \) and \( \tilde{M}^q(1) \) depends on the density, the generalized equations should be solved self-consistently. The solutions of the equations give us the \( N \) occupied quasi-particle states of the \( N \)-particle system, along with an infinite number of unoccupied quasi-particle states. To arrive at the one-body density, it is clear from Eqs. (2.26), (6.42), and (6.43) that [where \( M^{bg,b}(0) \) is the backward part of the universal background parametrization]

\[
\rho(\vec{r}) = \sum_{\nu(occ.)} \langle \vec{r} | X^q_{\nu}(\vec{r}) X^q_{\nu}^*(\vec{r}) | \vec{r} \rangle + \langle \vec{r} | \tilde{M}^{bg,b}(0) | \vec{r} \rangle
\]

\[
= \sum_{\nu(occ.)} X^q_{\nu}(\vec{r}) X^q_{\nu}^*(\vec{r}) + M^{bg,b}(0), \quad (6.50)
\]

where the wave functions \( X^q_{\nu}(\vec{r}) \) are related to the solutions of Eq. (6.47) by [see Eq. (6.44)]

\[
X^q_{\mu}(\vec{r}) = \int d^3 r' M^q_{\mu,\nu}(0) \chi^q_{\nu}(\vec{r}') \quad (6.51)
\]

The derivation and testing of a suitable parametrization will be the topic of a future study.
Chapter 7

Summary and future prospects.

The aim of this work is to reconcile two many-body schemes, namely the Green’s function formalism and the Density Functional Theory (DFT), which are generally applied to different categories of many-body systems. The fields of application only partly overlap. The first scheme was explained in general terms in chapter 2. Its main field of application consists of systems with a rather high degree of geometrical symmetry, such as nuclear matter, nuclei, the homogeneous electron gas, atoms, and condensed matter. The symmetry property is desirable because Green’s function calculations are quite expensive in computational terms. In the formalism, we use a Green’s function to describe the propagation of a particle or hole through the interacting many-body system. This Green’s function can be obtained by solving Dyson’s equation, which involves the self-energy to mediate what kind of two-body interactions are present in the system. The self-energy is in general a nonlocal (in coordinate space) and complex (in energy space) quantity, but can be expanded in a series in the two-body interaction (i.e. the Coulomb interaction for the present work). The self-energy series is truncated at some order $n$ and the result is substituted in Dyson’s equation, which is subsequently called the Dyson equation of order $n$.

As was discussed in chapter 2, the truncated self-energy depends on the Green’s function we are trying to find and therefore Dyson’s equation is to be solved self-consistently. If more terms are taken into account in the self-energy series, the solution of Dyson’s equation is more expensive, but more correlations between the particles are included in the scheme. The self-consistent process is an additional cost as well, but it makes the calculations independent of the initial guess and also it ensures that some basic conservation laws are obeyed, such as the number of particles.
In this work, Dyson’s equation is solved up to second order in the interaction for some closed-shell (He, Be, Ne, Mg, and Ar) and open-shell (B, C, N, O, and F) atomic systems. Atoms are a good choice for the present study because they form a group to which both of the two many-body schemes that are addressed in this work can be applied (another appropriate choice would be the electron gas or condensed matter).

The algorithm required to solve Dyson’s equation up to second order in the two-body interaction was developed in chapters 3 and 4 for closed- and open-shell systems respectively. Prior to the second-order scheme [termed the Dyson(2) scheme], the Dyson equation of first order [the Dyson(1) scheme, equivalent to the Hartree-Fock (HF) approximation] is solved in coordinate space. To obtain a complete HF basis in coordinate space, we need to describe the continuum properly. Since an exact treatment is prohibitive, we introduce a parabolic potential wall in the model at some distance from the nucleus in order to discretize the continuum. We can then find the eigenfunctions to this altered HF problem in coordinate space and construct a truncated but (quasi-)complete basis set in a fairly easy way. The Dyson(1) scheme amounts to solving the genuine (i.e. without wall) HF equations within this truncated set of wave functions. After this diagonalization, the newly obtained HF wave functions are used as a (quasi-complete) basis set to solve Dyson’s equation up to second order in the two-body interaction. To reduce the computational effort, we assumed that the Green’s function is diagonal within the HF basis set. We did not include screening nor relativistic effects in the scheme. To cope with the enormous increase in the number of poles of the Green’s function and the self-energy over the iterations in the second-order scheme, we adopt the BAGEL (BAsis GEnerated by Lanczos) algorithm. This scheme regroups the poles of the Green’s function and the self-energy into a smaller (fixed) amount of BAGEL poles. The regrouping process is performed such that the first few energy-weighted moments of the genuine spectral distribution and the BAGEL distribution remain conserved. In this way, the basic observables we usually calculate when performing Green’s function calculations (such as the ionization and the total energy) are unaffected. The results presented in chapters 3 and 4 demonstrate that the Green’s function calculations are capable of providing an accurate description of the atomic systems in this study. The calculated values of the ionization and the total energy reveal that the correlations embedded in the Dyson(2) scheme generate a shift from the HF value to the experimental outcome. For the open-shell atoms, another observable becomes of interest: the electron affinity. This quantity is a crucial test for the descriptive power of a many-body theory since correlations assume a very important role in the electron affinity. As was shown in chapter 4, the correlations of the Dyson(2) scheme are indispensable to account for a fair agreement with experiment. The success of Dyson(2) in predicting the electron affinity \textit{ab initio} is the more surprising since the Dyson(1) results predict a wrong value for the affinity and, as a consequence, do not provide a good starting point for the second-order scheme. Also, Green’s
function calculations adopt the so-called nonadiabatic approach: predictions of the ionization energy and the electron affinity are based on the calculation of the atom solely. This is opposed to the adiabatic approach where the total energy of both the atom and ion are optimized and subsequently subtracted. This latter approach generally gives better results than the nonadiabatic method because relaxation effects of the electron cloud can be taken into account more easily. It is unclear how the relaxation mechanism can be implemented within the self-consistent scheme of the Green's function calculation performed on the atom solely. Apart from energetic predictions, we can also derive the one-body electron density from the Green's function calculations, which is essential to make a connection with the second many-body scheme in this work, namely the Density Functional Theory.

The Green's function scheme can be elaborated in two ways. First, additional interactions can be included by taking into account higher-order (e.g. screening) diagrams and relativistic effects or by discarding the approximation that the Green's functions are diagonal in configuration space. This last extension may be especially beneficial for atoms like beryllium, where correlations are known to be quite important, causing additional interactions between different electron configurations in the atom. A second extension is to include systems other than atoms in the study. We could apply the Green's function scheme to ionic systems, like the iso-electronic series of helium, or to small molecules with cylindrical symmetry. Also, a high-level Green's function treatment of the homogeneous electron gas can be considered.

The advantage of the Green's function formalism is that it is very satisfying from a theoretical point of view: it is an ab initio scheme (no phenomenological input is required to start the algorithm) and the two-body effects can be identified very easily by means of Feynman diagrams. However, this microscopic approach is quite expensive numerically and therefore the application area of the formalism remains restricted to systems with a high degree of symmetry or a small number of particles. In this respect, the second many-body scheme of interest in this work, the Density Functional Theory (DFT), is quite the opposite: it is computationally (very) fast, can be applied to a variety of intricate many-body systems (even without any symmetry), but is not an ab initio scheme in a strict sense (i.e. although it can be based on ab initio grounds, its practical implementation often uses a semi-empirical input).

The density functional formalism was introduced in chapter 5 and uses the ground-state one-body density as a central quantity, rather than the Green's function or the many-body wave function as in standard quantum mechanics. It was demonstrated by Hohenberg and Kohn that the use of the ground-state density does not involve loss of information as compared to a wave-function based approach and that all observables can be expressed as functionals in the density. The use of the density, which depends on only three variables (regardless of the number of particles in the system), allows for the application of DFT to many-body systems with a large
number of electrons, such that intricate molecules are within reach. The density can be obtained from an Euler-Lagrange equation, which variationally minimizes the total energy of the many-electron system over all possible one-electron densities. The practical implementation of DFT, however, uses Schrödinger-like equations [the Kohn-Sham (KS) equations] which determine a set of single-particle orbitals. From these orbitals, we can calculate the ground-state one-body density of the interacting system. The KS equations turn the DFT-KS scheme into a computationally fast algorithm due to the use of the so-called exchange-correlation (xc) potential, which folds all two-body exchange and correlation effects into a one-body potential. This xc potential is defined as the functional derivative of the xc functional [a functional in the one-body density that includes all electron-electron interactions apart from the (classical) electrostatic repulsion of the electrons]. This xc functional is a universal quantity, i.e. it has the same form in terms of the density for any system that is governed by the Coulomb interaction. Unfortunately, the theory does not give clues on how to construct this xc functional. At the very best, there are merely some sum rules that can be derived within DFT for the exact xc functional. It is, however, quite tempting to try and find this universal functional, because then all electron systems could be solved in an exact way. Therefore, a large quantity of approximate forms have been developed, which implement exchange and correlation effects in the scheme in a more or less successful way. Most approximate functionals are constructed on semi-empirical grounds, e.g. starting from an expansion of the xc energy of the electron gas and adding parameters which are subsequently fitted to experimental data (involving a variety of systems). Sometimes, functionals are derived with parameters which are determined such that the basic rules for the exact xc functional are obeyed. These \textit{ab initio} functionals are much more satisfying from a theoretical point of view: universal functionals should be derived on universal principles. Therefore, scientists engage in the quest to find the exact xc potential for some simple model systems based on microscopic schemes. The efforts described in this work are an example of this approach: from the one-body densities calculated with the high-level Green’s function scheme, we can derive the corresponding xc potentials that DFT would require to describe that same atomic density.

The problem to find the xc potential that matches a given density is referred to as the inversion problem. A new and simple algorithm that performs this inversion process is discussed in chapter 6. The scheme is mainly based on numerical rather than physical grounds, but is much easier to implement than the standard algorithms to perform the inversion. In this work, the inversion scheme is applied to the atomic densities derived from our Green’s function calculations, but the algorithm can also be used on densities found by means of other methods such as quantum-Monte-Carlo simulations. Furthermore, we believe that the scheme can be extended to molecular systems as well because the physical principles underlying the scheme are quite universal. The xc potentials resulting from the inversion algorithm incor-
porate all correlations implemented in the Dyson(2) scheme. Since the correlations in this scheme can be identified straightforwardly by means of Feynman diagrams, we exactly know what kind of correlations are embedded within the potentials.

The exact xc potentials can be used in a variety of applications. We addressed two applications in chapter 6. First, the kinetic contribution to the correlation part of the xc functional can be derived. Since this quantity is the difference between two large quantities, it is known only in a very inaccurate manner. It is however of importance since it represents the correlations that are included in the interacting kinetic energy but that are not incorporated in the KS kinetic energy. Although the correlation effects are dominated by the exchange contribution, they are crucial for an accurate quantum-mechanical study of many-body systems by means of DFT. Therefore, the explicit calculation of the various correlation contributions to the generated xc potential (or the xc energy) is quite useful. The second application is to include the Dyson(2) xc potentials in a fitting procedure of a new or an existing functional. The advantage of including exact xc potentials in the fit next to energetic data is that the functional receives more information on how an accurate xc potential should behave. This may result in a behavior that yields e.g. improved optimized geometries of molecules when the functional is used in a DFT study. As described in chapter 6, this idea is implemented on the HCTH functional. Since we used the Dyson(2) predictions for the total energy as input for the energetic data, along with the exact potentials from the Dyson(2) scheme, the refit of the HCTH functional is based on purely ab initio grounds. In this work, the training set only consists of a small number of atomic systems and therefore, the resulting refit is not ready for applications. Future work can therefore be aimed at the increase of the training set, e.g. by means of the study of molecular and ionic systems. Eventually, a functional can be derived on fully ab initio grounds, which is able to make the same accurate predictions as the Green’s function method but that can be applied on a variety of intricate systems, beyond the reach of Green’s function theory. In a more general context, the assessment of present-day functionals by means of exact xc potentials can lead to a classification of the correlations embedded in these approximative forms, making it easier to predict what kind of functional is best suited for a particular system.

In the last section of chapter 6, we also sketched a generalization of the Kohn-Sham system, based on the Green’s function calculations. It consists of separating in the Green’s function the part that is specific for the many-body system at hand (the quasi-particle part) from the part that is universal for all electronic systems. For the universal component, a suitable parametrization is to be found, which can then be used in a generalized form of the KS equations. Because of the additional degrees of freedom in the generalized form, the modeling of the universal potential may be less troublesome than in conventional DFT. Devising and testing parametrizations of the universal background effects in the Coulomb interaction can also be the subject of a future study.
Samenvatting

Ab initio studie van Dichtheidsfunctionaaltheorie via Greense functies.

1 Algemene situering en samenvatting van het onderzoek.

De studie van veeldeeltjessystemen neemt een bijzondere plaats in in de fysica. Zoals genoegzaam bekend is, wordt de exacte oplossing van een systeem met een groot aantal deeltjes bemoeilijkt door de sterke uitbreiding van de beschikbare faseruimte voor de deeltjes. Algemeen dienen zich bij de studie van systemen met meer dan twee deeltjes numerieke methoden aan om een benaderende beschrijving van de banen van de deeltjes te geven. Ook in de studie van kwantummechanische systemen, zijn tal van benaderingsmethoden ontwikkeld om interagerende veeldeeltjessystemen te bestuderen. Deze methodes kunnen worden geklasseerd aan de hand van de empirische invloed die wordt toegelaten in de theorie. Wanneer het volledige formalisme wordt afgedaan enkel gebruik makende van de microscopische interactie tussen de samenstellende deeltjes, spreekt men van een ab initio theorie: er is geen enkele input van buiten af (dat wil zeggen dat er op geen enkele manier empirische informatie in de theorie wordt gesmokkeld). Verder zijn er nog de semi-empirische en de empirische methodes. Beide methodes zijn afhankelijk van experimentele informatie om het rekenschema te kunnen starten, maar in een verschillende gradatie. Algoritmes uit eerstgenoemde categorie vertrekken van een uitdrukking die is opgesteld vanuit de kwantummechanische beschrijving van het probleem, maar die een aantal te schatten parameters bevat. Deze parameters worden dan zo bepaald dat bepaalde experimentele grootheden worden gereguleerd. Empirische methodes daarentegen gebruiken een input die volledig op experimentele gronden is afgeleid.
De twee veeldeeltjestheorieën die in dit werk worden bestudeerd, het Greense functie formalisme en Dichtheidsfunctionaaltheorie (DFT), behoren respectievelijk tot de *ab initio* en de semi-empirische klasse van theorieën. Het Greense functie formalisme en DFT hebben elk hun specifieke toepassingsgebieden die slechts voor een deel overlappen. Door het succes van laatstgenoemd schema als een veeldeeltjestheorie wordt ook al geruime tijd geprobeerd een *ab initio* basis te geven aan DFT. Het is de bedoeling van dit werk om aan deze basis een bijdrage te leveren door systemen uit het overlappingsgebied tussen het Greense functie schema en DFT te bestuderen met behulp van Greense functie theorie en zo iets te leren over de semi-empirische input die DFT nodig heeft. We gaan nu al wat dieper in op de gedachtengang van beide methodes.

De Greense functie theorie beschrijft een veeldeeltjessysteem op microscopische schaal door, aan de hand van Greense functies, een deeltje in het intergerend veeldeeltjessysteem te volgen bij de beweging doorheen het systeem. Dit stelt ons in staat om een zuiver theoretische beschrijving te geven van het kwantum systeem, hoewel het uiteraard een lastige en computationeel veeleisende manier van werken is. Vandaar dat het toepassingsgebied van de Greense functie methode zich voor namelijk beperkt tot systemen met een zekere vorm van symmetrie, zoals kernmatie, kernen, het homogene elektron gas, atomen en vaste stoffen. De één deeltje Greense functie wordt verkregen door het oplossen van Dyons vergelijking. Deze bevat een speciale operator, de zelf-energie, die verantwoordelijk is voor de beschrijving van alle interacties die het deeltje op weg door het systeem ondergaat. De zelf-energie is een niet-lokaal (in de coördinatenruimte) en een energieafhankelijke (in de energieruimte) grootheid. Gezien de grote complexiteit van deze operator, wordt deze meestal in een stortingsreeks in de tweedeleljes interactie (in dit werk de Coulomb wisselwerking) ontwikkeld en dan afgebroken na orde \( n \). De bekomen expansie voor de zelf-energie wordt dan in de Dyson vergelijking gestopt. Het resultaat wordt de Dyson vergelijking van orde \( n \) genoemd. Zoals zal worden besproken in paragraaf 2, hangt de getruncerde zelf-energie ook nog af van de Greense functie die we proberen te zoeken met behulp van Dysons vergelijking. Dit betekent dat het oplossen van de Dyson vergelijking tot op orde \( n \) in de interactie op een *zelf-consistente manier* moet gebeuren (zie paragraaf 2). Wanneer meer termen in de expansie van de zelf-energie worden meegenomen, wordt de oplossing van de Dyson vergelijking moeilijker, maar de beschrijving van het veeldeeltjessysteem is wel vollediger. Bij een gegeven truncatie orde brengt de zelf-consistente behandeling van Dysons vergelijking op zich al grote complicaties met zich mee. De zelf-consistentie zorgt er echter wel voor dat de uiteindelijke oplossing onafhankelijk is van de *ansatz* die is gebruikt om de zelf-energie initieel mee te evalueren en dat aan bepaalde behoudswetten wordt voldaan (zoals het behoud van deeltjesaantal). In dit werk wordt de reeksontwikkeling van de zelf-energie afgebroken na tweede orde en wordt de corresponderende Dyson vergelijking opgeloos voor gesloten en open schil atomen. Atomen vormen een goede keuze als studiemateriaal omdat zowel
1. Algemene situering en samenvatting van het onderzoek.

Greense functies als DFT erop kunnen worden toegepast (andere kandidaten zijn het elektron gas en vaste stoffen). Zodoende hebben we de mogelijkheid om vanuit een hoogwaardige beschrijving van de testsystemen met behulp van Greense functies conclusies te trekken over de kwaliteit van de beschrijving van dezelfde systemen met DFT. We gaan nu wat dieper in op de benaderingswijze van DFT.

Dichtehedsfunctionaaltheorie gebruikt de ééndeeltijdsdichtheid in de grondtoestand (kortweg als de dichtheid aangeduid) als centrale variabele, van waaruit alle andere observabelen kunnen worden berekend. We kiezen dus direct een waarnembare groothed als centrale variabele, in tegenstelling tot b.v. de totale golffunctie van het veeldeltjessysteem in standaard kwantummechanica. Zoals zal worden besproken in paragraaf 5, gaat bij deze keuze geen informatie verloren, hoewel de dichtheid maar drie variabelen heeft, veel minder dan een typische veeldeltjegolffunctie (3N, met N het aantal deeltjes in het systeem). Hierdoor is DFT zeer geschikt om ingewikkeldere structuren aan te pakken (bijvoorbeeld molecules bestaande uit een groot aantal atomen, zonder enige vorm van symmetrie). Eens de dichtheid gekend, kan iedere observabele van het veeldeltjessysteem worden berekend als een functionaal in de dichtheid. Binnen DFT kan de dichtheid in de grondtoestand bekomen worden door het oplossen van de Euler-Lagrange vergelijking die variationeel de totale energie van het systeem minimaliseert over alle mogelijke ééndeeltjedichtheden die in het systeem kunnen voorkomen. Praktisch gebeurt een DFT berekening echter via het Kohn-Sham (KS) schema, dat een stekel Schrödingerrachtige vergelijkingen omvat waarvan de oplossingen (de Kohn-Sham ééndeeltjesorbitals) de ééndeeltjedichtheid van het interacterend systeem geven. Het KS schema zorgt ervoor dat DFT een computationeel snel schema is door het introduceren van de uitwisselingscorrelatiepotentiaal, een ééndeeltjepotentiaal die in principe alle tweedeeltjejseffecten afkomstig van de Coulomb wisselwerking in zich draagt. De uitwisselingscorrelatiepotentiaal wordt binnen het DFT formalisme gedefinieerd als de functionaal afgeleide van de uitwisselingscorrelatiefunctionaal. Deze functionaal is universeel, dat wil zeggen dat deze dezelfde vorm heeft in termen van de dichtheid in om het even welk systeem waarin de Coulomb wisselwerking werkzaam is (bijvoorbeeld een atoom, molecule of vaste stof). Jammer genoeg geeft DFT geen aanwijzingen over hoe deze functionaal moet worden geconstrueerd, er zijn hoogstens enkele somregels op te stellen waaraan de functionaal moet voldoen. Het is echter wel heel verleidelijk om deze universele functionaal te zoeken, want als we die hebben zou oender welk veeldeltjesprobleem met Coulomb interacties exact kunnen worden opgelost. In de praktijk wordt er gebruik gemaakt van benaderende functionalen die de uitwisselings- en oorrelatiebijdragen tot op zekere hoogte in zich dragen. Er zijn tal van benaderingen bekend die elk goed werken voor een specifieke klasse van systemen. Meestal worden de functionalen afgeleid op semi-empirische gronden, waarbij men vertrekt van bijvoorbeeld de expansie van de totale energie per deeltje van het elektron gas en aan die uitdrukking parameters toevoegt die dan aan een ruime "training set" van atomen, ionen en molecules worden gefit. Sommige functionalen
bestaan echter uit een parameter set die zo werd gekozen dat aan enkele exacte somregels voor de uitwisselingscorrelatiefunctiaal wordt voldaan. Deze laatste manier van werken geeft vanuit theoretisch standpunt meer voldoening, gezien het een \textit{ab initio} aanpak is: universele functionalen zouden moeten worden afgeleid op basis van universele principes. In deze optiek is het dan ook interessant om voor bepaalde eenvoudige testsystemen met behulp van schema’s buiten DFT na te gaan hoe de uitwisselingscorrelatiefunctiaal of -potentiaal eruit ziet. In dit kader situeert zich het huidig onderzoek: aan de hand van de Greense functie methode kunnen we de één- en delftjesdichtheid bepalen voor de grondtoestand van enkele atomaire systemen. We moeten dan de uitwisselingscorrelatiepotentiaal vinden die DFT zou nodig hebben om dezelfde grondtoestandsdichtheid te beschrijven: dit is het zogenaamde inversie probleem. In paragraaf 6 wordt een nieuw en eenvoudig algoritme geschetst om het inversieproces uit te voeren. Van de resulterende potentiaal weten we dan tot in detail welke correlaties zijn ingebouwd (namelijk die van het geavanceerde Greense functie schema). Deze exacte potentialen kunnen dan b.v. gebruikt worden bij het herfitten van bestaande functionalen of bij het opstellen van een nieuwe funtionaal op volledig \textit{ab initio} gronden. Op die manier kunnen de Greense functie berekeningen bijdragen tot een microscopische basis voor DFT functionalen en zorgen voor een eventuele systematische aanpak om functionalen op te stellen. Meer algemeen kunnen de exacte potentialen worden aangewend om na te gaan welke correlaties precies ingebouwd zijn in de benaderende functionalen van DFT. Dit inzicht kan dan worden gebruikt om te voorspellen welke klasse van functionalen het best is geschikt om een bepaald probleem aan te pakken.

2 Het Greense functie formalisme.

We gaan nu over tot een samenvatting van het Greense functie formalisme in een vorm die relevant is voor dit werk. Hoewel Greense functies op tal van systemen kunnen worden toegepast, zullen we ons hier beperken tot systemen waarin de Coulombkracht werktzaam is. Een uitvoeriger uiteenzetting van het formalisme kan worden gevonden in hoofdstuk 2.

In een veeldeeltjes-schema wordt vaak gebruik gemaakt van tweede kwantizatie. De hamiltoniaan van een veeldeeltjesensemble waarin de deeltjes interageren door middel van de Coulomb wisselwerking is in tweede kwantizatie (we onderscheiden operatoren in tweede van die in eerste kwantizatie door een caret ^) 

\[
\hat{H} = \hat{H}_0 + \hat{W} = \int dx c^\dagger(x) H_0(x) c(x) + \frac{1}{2} \int dx dx' c^\dagger(x) c^\dagger(x') W(x, x') c(x') c(x), \tag{1}
\]

waar \(\hat{H}_0\) de kinetische energie en externe ééndeeltjespotentialen (zoals de interactie tussen kern en elektronen) omvat. De tweedeeltjesinteractie \(\hat{W}\) zal in dit werk steeds
2. Het Greense functie formalisme.

De Coulomb interactie zijn. De ruimtecoördinaten worden aangeduid met \(x\). Indien nodig kan in deze notatie ook de spinvrijheidsgraad worden opgenomen. De operator \(c_t(x)\left|e(x)\right.\) is de creatie (anihilatie) operator in het Schrödingerbeeld van een deeltje op plaats \(x\). Verder vermelden we nog dat alle formules en resultaten gegeven worden in het atomaire eenhedenstelsel, waarin b.v. de gereduceerde Planck constante \(\hbar = 1\) en de Bohrse straal \(a_0 = 1\) worden gesteld (zie App. A).

In de coördinaten-tijd representatie, wordt de één-deeltje Greense functie gedefinieerd als [2]:

\[
G(x,t;x',t') = -i \left\langle 0(A) \left| \mathcal{T} \left[ c_H(x,t)c_H^\dagger(x',t') \right] \right| 0(A) \right\rangle.
\] (2)

De exacte grondtoestand van het \(A\)-deeltjessysteem wordt aangeduid met \(\left| 0(A) \right\rangle\) en \(c_H(x,t)\left| c_H^\dagger(x,t) \right\rangle\) stelt de Heisenberg annihilatie (creatie) operator voor, die een deeltje op punt \((x,t)\) annihilt (creëert). In deze definitie komt ook de tijdscoordinaat \(T\) voor, die de Heisenberg operatoren ordent volgens hun tijdscoördinaat; een operator met een grotere tijdscoördinaat wordt links van een operator met een kleinere tijdscoördinaat geplaatst. Voor fermion operatoren brengen elk van deze permutaties ten gevolge van de anti-commutatie relaties een extra minteken met zich mee afhankelijk van het aantal verwisselingen nodig om tot een correcte tijdsordering te komen, kan globaal een extra minteken opduiken. Schrijven we de tijdscoordinaat operator expliciet uit, dan bekomen we [waarbij ondersteld wordt dat \(\left| 0(A) \right\rangle\) genormeerd is op 1 en waarbij \(\theta(x)\) de stapfunctie voorstelt]

\[
G(x,t;x',t') = -i \langle 0(A) \left| c_H(x,t)c_H^\dagger(x',t') \right| 0(A) \rangle \theta(t - t') + i \langle 0(A) \left| c_H^\dagger(x',t')c_H(x,t) \right| 0(A) \rangle \theta(t' - t).\] (3)

Uit deze gedaante van de Greense functie kunnen we gemakkelijk een fysische interpretatie afleiden. Voor \(t > t'\), beschrijft de Greense functie een deeltje dat bovenop de grondtoestand van het \(A\)-deeltjessysteem wordt gecreëerd, en dat propageert van het punt \((x',t')\) waar het is gecreëerd tot de annihilatie op \((x,t)\), waar het systeem terugkeert naar de grondtoestand \(\left| 0(A) \right\rangle\). Bij deze propagatie interageert het deeltje met de rest van het veeldeeltjessysteem, zoals wordt uitgedrukt door de tijdsevolutie van de Heisenberg operatoren \(c_H(x,t) = e^{iHt}c(x)e^{-iHt}\). Analoog kan een interpretatie gevonden worden in het geval \(t' > t\): de Greense functie beschrijft dan de propagatie van een gat in het \(A\)-deeltjessysteem.

In dit werk wordt gebruik gemaakt van de Greense functie in de configuratie-energie representatie i.p.v. de coördinaten-tijd representatie. Een dergelijke transformatie kan worden doorgevoerd door Fouriertransformatie en vereist dat de hamiltoniaan tijdsonafhankelijk is (zodat de Greense functie enkel afhankt van het tijdsverschil \(t - t'\)). De Greense functie krijgt dan de gedaante (de labels \(\alpha, \beta, \ldots\) duiden de
kwantumgehalten aan de ééndeeftjesorbitalen in een complete en orthonormale basis en \( \eta > 0 \) vervult de rol van een infinitesimale convergentie parameter)

\[
G_{\alpha\beta}(E) = \langle 0(A) | c_\alpha \frac{1}{E - \hat{H} + E_{0(A)} + i\eta} c_\beta^\dagger + c_\beta \frac{1}{E + \hat{H} - E_{0(A)} - i\eta} c_\alpha | 0(A) \rangle, \tag{4}
\]

waarbij we een gelijkaardige interpretatie kunnen hechten aan de twee termen in het rechterlid als die in de coördinaten-tijd representatie voor vergelijking (3) is gegeven.

De creatie operator \( c_\alpha^\dagger \) kan worden gerelateerd aan zijn coördinaten tegenhanger door de uitdrukking \( c_\alpha^\dagger (x) = \sum_\alpha \phi_\alpha (x) c_\alpha \), waar \( \phi_\alpha (x) \) de orbitaal is in de complete set aan toestanden die correspondeert met het label \( \alpha \). Een gelijkaardige uitdrukking geldt voor de annihilatie operator \( c_\alpha \).

In de configuratieruimte krijgt de hamiltoniaan volgende vorm

\[
\hat{H} = \hat{H}_0 + \hat{W} = \sum_{\alpha, \beta} \langle \alpha | H_0 | \beta \rangle c_\alpha^\dagger c_\beta + \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} \langle \alpha \beta | W | \gamma \delta \rangle_{as} c_\alpha^\dagger c_\beta^\dagger c_\gamma c_\delta,
\]

waarbij wordt benadrukt dat het matrixelement van de Coulomb interactie gantsymmetriseerd is \( \langle \alpha \beta | W | \gamma \delta \rangle_{as} = \langle \alpha \beta | W | \gamma \delta \rangle - \langle \alpha \beta | W | \delta \gamma \rangle \).

Vanuit vergelijking (4) kunnen we een belangrijke alternatieve gedaante afleiden voor de Greense functie door een complete set van orthonormale toestanden van het \((A + 1)\)- en \((A - 1)\)-deeltjessysteem in te voegen:

\[
\sum_{N(A+1)} | N(A + 1) \rangle \langle N(A + 1) | = 1, \quad \sum_{N(A-1)} | N(A - 1) \rangle \langle N(A - 1) | = 1. \tag{6}
\]

Op die manier bekomen we de **Lehmann representatie** voor de Greense functie

\[
G_{\alpha\beta}(E) = \sum_{N(A+1)} \frac{\langle 0(A) | c_\alpha \frac{1}{E - E_{N(A+1)} + E_{0(A)} + i\eta} c_\beta^\dagger | N(A + 1) \rangle \langle N(A + 1) | c_\beta^\dagger | 0(A) \rangle}{E - E_{N(A+1)} + E_{0(A)} + i\eta} + \sum_{N(A-1)} \frac{\langle 0(A) | c_\alpha \frac{1}{E + E_{N(A-1)} - E_{0(A)} - i\eta} c_\alpha^\dagger | 0(A) \rangle}{E + E_{N(A-1)} - E_{0(A)} - i\eta}. \tag{7}
\]

De som over de \((A \pm 1)\) toestanden bevat naast een som over het discrete spectrum ook nog een integratie over de continuïm orbitalen.

Hoewel de Lehmann representatie van de Greense functie abstract aandoet, bevat deze belangrijke grootheden die experimenteel kunnen worden gemeten. De polen van de Greense functie geven de energieën \( E_{N(A \pm 1)} \) van de eigentoestanden in het \((A \pm 1)\)-elektron systeem, relatief t.o.v. de grondtoestandsenergie van het \( A \)-elektron atoom, d.w.z. \( E_{0(A)} - E_{N(A+1)} \) of \( E_{N(A-1)} - E_{0(A)} \). Twee van deze
polen zijn van speciaal belang, namelijk deze waarbij enkel verschillen tussen grondtoestanden worden beschouwd: de elektronenaantrekkingsenergie kan worden gedefinieerd als (cf. [12]) \( A = E_{0(A)} - E_{0(A+1)} \) en de eerste ionisatie energie als \( I = E_{0(A-1)} - E_{0(A)} \).

Een tweede belangrijke klasse van experimentele grootheden in de Lehmannen representatie zijn de residu’s van de polen, die verband houden met de Feynman-Dyson amplitudes [8] \( \langle N(A-1) \mid c_\alpha \mid 0(0) \rangle \) en \( \langle 0(0) \mid c_\alpha \mid N(A+1) \rangle \). Het kwadraat van de \( N(A-1) \) amplitude kan worden genomen in (\( e^2 \)) experimenten, waarbij een elektron wordt verstrooid aan een atoom met een voldoende hoge energie om één van de elektronen van het atoom te strippen (zie ook de experimentele resultaten in paragraaf 3 en 4).

Voor later gebruik vermelden we ook de ***deeltje spectrale functie***

\[
S^\h_\alpha(E) = \sum_{N(A+1)} \mid \langle 0(A) \mid c_\alpha \mid N(A+1) \rangle \mid^2 \delta \left( E - E_{N(A+1)} + E_{0(A)} \right),
\]

en de ***gat spectrale functie***:

\[
S^\h_\alpha(E) = \sum_{N(A-1)} \mid \langle 0(A) \mid c_\alpha^\dagger \mid N(A-1) \rangle \mid^2 \delta \left( E + E_{N(A-1)} - E_{0(A)} \right).
\]

De fysische interpretatie van de spectrale functie is de kans om een deeltje toe te voegen aan of te verwijderen uit de gecorreleerde grondtoestand van het \( A \)-deeltjesysteem en het resulterende systeem in een energietoestand \( E \) te vinden.

We merken nog op dat we met behulp van de Greense functie de verwachtingswaarde van een ééndeeltjess operator \( \hat{O}^{(1)} \) kunnen berekenen via

\[
\langle 0(A) \mid \hat{O}^{(1)} \mid 0(A) \rangle = \sum_{\alpha \beta} \langle \alpha \mid \hat{O} \mid \beta \rangle \langle 0(A) \mid c_\alpha^\dagger c_\beta \mid 0(A) \rangle
\]

\[
= \sum_{\alpha \beta} \langle \alpha \mid \hat{O} \mid \beta \rangle \int_{-\infty}^{\infty} \frac{dE}{2\pi i} e^{iKE} G_{\beta \alpha}(E),
\]

waar de factor \( e^{iKE} (\zeta > 0) \) ervoor zorgt dat alleen het achterwaartse deel van de Greense functie [de tweede term in vergelijking (4)] geselecteerd wordt. Een speciaal voorbeeld van deze uitdrukking is de ééndeeltjesdichtheid

\[
\langle 0(A) \mid \hat{\rho} \mid 0(A) \rangle = \sum_{\alpha \beta} \langle \alpha \mid \delta_{\alpha \beta} \mid \beta \rangle \int_{-\infty}^{\infty} \frac{dE}{2\pi i} e^{iKE} G_{\beta \alpha}(E)
\]

\[
= \sum_{\alpha} \int_{-\infty}^{\infty} \frac{dE}{2\pi i} e^{iKE} G_{\alpha \alpha}(E).
\]

In het algemeen hebben we een tweedeeltje Greense functie nodig om verwachtungs waarden te berekenen van tweedeeltjes operatoren, zoals de hamiltoniaan (1).
De totale energie vormt echter een speciaal geval en zoals we verder zullen zien kunnen we inderdaad met de ééndelige Greense functie die in dit werk wordt beschouwd de totale energie berekenen.

Zoals uitgelegd in hoofdstuk 2, kan de Greense functie van het interagerend systeem worden ontwikkeld in een reeks in de tweedeeljesinteractie. Het bijzondere aan het werken met Greense functies is dat de corresponderende stokersrekenings gemakkelijk kan worden beschreven a.h.v. Feynman diagrammen (een overzicht van de relevante Feynman regels wordt gegeven in App. B). De stokersreeks kan handig worden gehergroeperd door het concept van de (irreducibele) zelf-energie $\Sigma_{\alpha\beta}(E)$ en een goed-gekozen niet-interagerend systeem in te voeren dat als start dient om het interagerend systeem aan te pakken. Het resultaat van het hergroeperen is een vergelijking die de Greense functie van een deel shrine (of get) in een interagerend systeem schrijft als de Greense functie van het niet-interagerende systeem en een correctieterm die de zelf-energie bevat. Deze niet-interagerende Greense functie $G_{\alpha\beta}^{(0)}(E)$ wordt gedefinieerd als in vergelijking (4), waarbij $|0(A)|$ nu de grondtoestand van het niet-interagerend systeem wordt. De (irreducibele) zelf-energie omvat alle interacties die optreden in het interagerend systeem, maar die niet zijn opgenomen in het niet-interagerend systeem. De bekomen vergelijking wordt de Dyson vergelijking genoemd. In Feynman diagrammen ziet deze vergelijking er uit als in Fig. 1.

![Dyson Vergelijking](image)

**Figuur 1:** De Greense functie bepaald door Dyson's vergelijking.

Hierbij wordt de Greense functie van het interagerend systeem aangeduid met een dubbele lijn, die van het niet-interagerend systeem met een enkele lijn en de (irreducibele) zelf-energie met een ellips die in het centrum het symbool $\Sigma$ bevat. In analytische vorm krijgen we in de configuratie-energie ruimte voor de Dyson vergelijking

$$G_{\alpha\beta}(E) = \delta_{\alpha\beta} G_{\alpha\beta}^{(0)}(E) + \sum_{\alpha'\beta'} \delta_{\alpha\alpha'} G_{\alpha\alpha'}^{(0)}(E) \Sigma_{\alpha'\beta'}(E) G_{\beta'\beta}(E).$$  \hspace{1cm} (12)

De expansie voor de zelf-energie wordt gegeven in Fig. 2 in Feynman diagrammen. Meestal zullen we aannemen dat de Greense functies diagonaal zijn in de basis die wordt gebruikt om de configuratie ruimte op te bouwen. Daardoor wordt ook de
zelf-energie diagonaal en kunnen we Eq. (12) herschrijven als

$$G_{\alpha\alpha}(E) = \frac{1}{G_{\alpha\alpha}^{(0)}(E)^{-1} - \Sigma_{\alpha\alpha}(E)}.$$  \hfill (13)

Zoals al aangegeven in de inleiding tot dit hoofdstuk, is de zelf-energie afhankelijk van de Greense functie van het interacterend systeem. Dit is de prijs die men bij het hergroeperen van de storengskreeks voor de Greense functie moet betalen om tot een elegante vorm als in Fig. 1, gecombineerd met Fig. 2 te komen.

\begin{equation}
\begin{array}{c}
\text{Figuur 2: Expansie voor de irreducibele zelf-energie.}
\end{array}
\end{equation}

De praktische werkwijze om Dysons vergelijking op te lossen ligt nu voor de hand. Eerst truceren we de zelf-energie van Fig. 2. Aangezien de zelf-energie afhing van de Greense functie die we proberen te berekenen, moeten we de corresponderende Dyson vergelijking zelf-consistent oplossen. Eerst maken we een initiële schatting voor de Greense functie (b.v. gebaseerd op de Greense functie voor een vrij deeltje) en evalueren daarmee de zelf-energie. Met deze schatting voor de zelf-energie lossen we de Dyson vergelijking op om een update te krijgen voor de Greense functie, waarmee we een nieuwe evaluatie maken van de zelf-energie. We lossen de corresponderende Dyson vergelijking op en herhalen de cyclus tot de Greense functie van een bepaalde iteratie samenvalt met die van de vorige iteratie.

In dit werk zijn enkel eerste en tweede orde contributies tot de zelf-energie van belang. De eerste orde term in de zelf-energie is equivalent met de Hartree-Fock (HF) benadering (het eerste diagram in Fig. 2). In deze benadering krijgt de Dyson vergelijking volgende vorm

\begin{equation}
\begin{align}
G_{\alpha\alpha}^{(1)}(E) &= \frac{1}{G_{\alpha\alpha}^{(0)}(E)^{-1} - \Sigma_{\alpha\alpha}^{(1)}(E)}, \\
&= \frac{\theta(\epsilon_{F\alpha}^{HF} - \epsilon_F)}{E - \epsilon_{F\alpha}^{HF} + i\eta} + \frac{\theta(\epsilon_F - \epsilon_{F\alpha}^{HF})}{E - \epsilon_{g\alpha}^{HF} - i\eta},
\end{align}
\end{equation}

waar $G_{\alpha\alpha}^{(0)}(E)$ de propagator is die een vrij deeltje beschrijft, $\epsilon_F$ de Fermi energie van het systeem voorstelt (gedefinieerd als gemiddelde tussen hoogste bezet en laagste
onbezet energieniveau) en waar \( e^H_{\alpha} \) de ééndaltesenergie van het deeltje of het gat is dat door de Grense functie wordt beschreven.

Uit het Feynman diagram voor de eerste orde zelf-energie halen we volgende analytische uitdrukking

\[
\Sigma^{(1)}_{\alpha\alpha}(E) = (-1) \frac{i}{2\pi} \sum_{\beta} \langle \alpha\beta | W | \alpha\beta \rangle_{as} \int dE' e^{iE'f} G^{(1)}_{\beta\beta}(E'),
\]

waaruit duidelijk blijkt dat \( \Sigma^{(1)}_{\alpha\alpha}(E) \) eigenlijk energie-onafhankelijk is (conform met de eigenschap dat het HF gemiddeld vekl stationair is).

De tweede orde zelf-energie term is wel energie-afhankelijk. Het tweede diagram in Fig. 2 geeft ons volgende analytische uitdrukking

\[
\Sigma^{(2)}_{\alpha\alpha}(E) = \frac{1}{(2\pi)^2} \sum_{\beta_1,\beta_2} \frac{1}{2} | \langle \alpha\beta_3 | W | \beta_1\beta_2 \rangle_{as} |^2 \\
\int dE_1 \int dE_2 G^{(2)}_{\beta_1\beta_1}(E - E_1 + E_2) G^{(2)}_{\beta_2\beta_2}(E_1) G^{(2)}_{\beta_3\beta_3}(E_2).
\]

(16)

In een tweede orde berekening wordt typisch de HF benadering als startpunt gebruikt i.p.v. de vrije propagator \( G^{(0)} \):

\[
G^{(2)}_{\alpha\alpha}(E) = \frac{1}{G^{(0)}_{\alpha\alpha}(E) - \Sigma^{(1)}_{\alpha\alpha} - \Sigma^{(2)}_{\alpha\alpha}(E)} \\
= \frac{1}{G^{(1)}_{\alpha\alpha}(E) - \Sigma^{(2)}_{\alpha\alpha}(E)} \\
= \frac{1}{E - e^H_{\alpha} - \Sigma^{(2)}_{\alpha\alpha}(E)}.
\]

(17)

In de volgende paragrafen gaan we na hoe deze vergelijking kan worden opgelost voor atomaire systemen.

3 Zelf-consistente oplossing van Dyson’s vergelijking voor gesloten schil atomen.

Eerst bespreken we de oplossing van Dyson’s vergelijking voor gesloten schil atomen. De uitbreiding naar open schil atomen volgt in paragraaf 4. Zoals vermeld in de vorige paragraaf lossen we eerst de HF vergelijkingen op vooraleer de Dyson vergelijking tot op tweede orde wordt aangepakt. In onderdeel 3.1 wordt uitgelegd hoe de HF vergelijkingen kunnen worden opgelost in de coördinaten-energie representatie. In deze stap construeren we een (bijna) complete basis aan HF orbitalen die dan kan worden gebruikt om de Dyson vergelijking op te lossen in de configuratie-energie representatie tot op tweede orde in de tweedeeltjesinteractie (de zelf-energie wordt
getruncateerd na de tweede orde term. De oplossing van de tweede orde Dyson vergelijking wordt uitgelegd in onderdeel 3.2. In onderdeel 3.4 worden dan enkele resultaten besproken.

### 3.1 Numerieke oplossing van Dysons vergelijking tot op eerste orde in de interactie.

De HF vergelijkingen die we moeten oplossen hebben in de coördinaten-energie ruimte volgende gedaante (in atomaire eenheden)

\[
\left\{ -\frac{1}{2}\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - \frac{Z}{r} + V_H(r) \right\} P_{nl}(r) - [\tilde{V}_F P_{nl}](r) = \epsilon_{nl}^{HF} P_{nl}(r),
\]

waarbij \( n \) het hoofdkwantumgetal is, \( l \) het orbitaal kwantum getal en \( Z \) het atoomgetal (aangezien we werken met neutrale atomen is dit ook het aantal elektronen). De radiale golffunctie \( P_{nl}(r) \) (corresponderend met de eigenenergie \( \epsilon_{nl}^{HF} \)) is genormeerd als \( \int_0^\infty dr P_{nl}(r) P_{nl'}(r) = \int_0^\infty dr r^2 \phi_{nl}(r) \phi_{nl'}(r) = \delta_{nn'} \delta_{ll'} \). De Hartree potentiële kan tot volgende gedaante worden omgevormd

\[
V_H(r) = \sum_{n'l'm'_{\text{occ}}} \sum_{s'} \int d^3r' \phi_{n'l'}(r')^2 | Y_{m_{l'}}(\Omega') \|^2 | \chi_{m_{s'}}(s') |^2 \frac{1}{|r - r'|},
\]

\[
= \sum_{n'l'} (2l' + 1) \int d^3r' P_{n'l'}(r')^2 + \int_0^\infty dr' \frac{1}{r'} P_{n'l'}(r')^2,
\]

met \( m_{s'} \) de projectie van het orbitaal draaimoment \( l' \) (de spin \( s' \)), \( Y_{m_{l'}}(\Omega) \) de sferische harmoniek corresponderend met \( (l, m_l) \) en \( \chi_{m_{s'}}(s') \) de spinor eigenfunctie. De Fock potentiële wordt

\[
[\tilde{V}_F P_{nl} \chi_{m_s}](r, s) = \int d\Omega \ Y_{m_l}^*(\Omega) \ [\tilde{V}_F P_{nl} Y_{m_l}^l(\Omega,\Omega) \chi_{m_s}](r, \Omega, s)
\]

\[
= \int d\Omega \ Y_{m_l}^*(\Omega) \sum_{n'l'm'_{\text{occ}}} \sum_{s'} \int d^3r' d^3\Omega' \ P_{n'l'}(r') P_{nl}(r) P_{nl'}(r') Y_{m_{s'}}(s') \chi_{m_{s'}}(s') \chi_{m_{s'}}(s)
\]

\[
= \sum_{n'l'm'_{\text{occ}}} \delta_{m_s,m_s'}(2l' + 1) \sum_{L=0}^\infty \left( \begin{array}{ccc} l & l' & L \\ 0 & 0 & 0 \end{array} \right)^2 P_{n'l'}(r) \chi_{m_{s'}}(s')
\]

\[
\left[ \frac{1}{r' + r} \int_0^\infty dr' r'^L P_{n'l'}(r') P_{nl}(r) + r'^L \int_0^\infty dr' \frac{1}{r' + r} P_{n'l'}(r') P_{nl}(r') \right].
\]

We benadrukken dat bovenstaande uitdrukkingen enkel gelden voor gesloten schil atomen. Volgende randvoorwaarden worden opgelegd aan de HF vergelijkingen

\[
P_{nl}(0) = 0, \quad P_{nl}(r \to \infty) \to 0.
\]
Om de HF vergelijkingen met bijpassende randvoorwaarden op te lossen in de coördinatenruimte, voeren we eerst een goed gekozen rooster in voor de radiale coördinaat \( r \). In een atomair systeem hebben we meer punten nodig dichtbij de kern, waar de afgeleide van de golffunctie sterker fluctueert dan verderaf. Een equidistante sampling van de variabele \( r \) levert bijgevolg geen adequaat grid. Daarom wordt vaak een transformatie van \( r \) naar de zogenoemde *logaritmische variabele* 
\[
\rho = \frac{1}{c_1} \ln \left( \frac{r}{a_0} \right)
\]
uitgevoerd. Hierbij kiezen we \( 0 < \rho \leq 1 \) en \( a_0 = r_{\min} \), \( c_1 = \ln \frac{r_{\max}}{r_{\min}} \), zodat \( r_{\min} \leq r \leq r_{\max} \). In dit werk worden de waarden \( r_{\min} = 10^{-6} \) en \( r_{\max} = 50 \) atomaire eenheden gebruikt. Een equidistante sampling van het logaritmische grid levert punten in de \( r \) ruimte die verder uit elkaar liggen naarmate \( r \) groter wordt en dus uitermate geschikt voor atomaire systemen.

Aangezien in de tweede orde Dyson vergelijking zowel deeltjes- als gatpropagatoren optreden en we deze tweede orde vergelijking oplossen in een basis van HF orbitalen, moeten we de HF vergelijkingen zowel voor bezette als onbezette orbitalen oplossen. Daar de onbezette orbitalen in het continuüm deel van het spectrum liggen en een exacte behandeling van het continuüm numeriek moeilijk ligt, moeten we een manier vinden om het continuüm te discretiseren. In dit werk wordt dit opgelost door artificieel een paraboolische potentiaal toe te voegen aan de HF hamiltoniaan. Deze 'muur' wordt op een vloeibare manier aangeschakeld vanaf afstand \( R \):
\[
U_l(r) = C_l \theta(r - R_l) (r - R_l)^2.
\]

Het bleek numeriek voordelig te zijn om een muur in te voeren per angular moment \( l \), vandaar het subscript \( l \).

Het eigenlijke algoritme om Dysons vergelijking zelf-consistent op te lossen tot op eerste orde in de interactie bestaat uit drie stappen. Eerst lossen we de echte HF vergelijkingen (d.w.z. de HF vergelijkingen zonder muur) zelf-consistent op, maar wel enkel voor de gebonden toestanden. Op die manier ligt het HF gemiddeld veld voor het atoom vast. Nu voegen we de muur toe aan deze externe potentiaal en lossen de eendeljesvergelijkingen op die horen bij de gemodificeerde HF potentiaal voor zowel de bezette als de onbezette toestanden. Alle toestanden in dit probleem zijn door toedoen van de optuivende muur gebonden toestanden. Uiteraard moet tijdens het integratie proces het aantal toestanden dat wordt berekend enig wordt gehouden. Tijdens de berekeningen in dit werk werd er wel op toegezien dat in deze truncatie een voldoende aantal "continuüm" toestanden wordt meegenomen zodat de basis set compleet blijft voor praktische doeleinden. De golffuncties die we op het einde van de tweede stap bekomen, dragen vanzelfsprekend sporen in zich van de artificiële muur. Om die invloed weg te werken, lossen we het oorspronkelijk HF probleem (zonder muur) nog eens zelf-consistent op voor zowel de gebonden als de continuüm toestanden, maar dit keer in de (bijna) complete basis die in de tweede stap is genereerd. De compleetheid van de basis kan worden getest door de gebonden eigenwaarden uit de derde stap te vergelijken met die van de eerste
stap, die in het geval van een complete basis uiteraard moeten samenvallen. De zelf-consistente oplossing van de HF vergelijking in de derde stap wordt in het vervolg het Dyson(1) schema genoemd. Op het einde van de derde stap hebben we dan een nieuwe (bijna) complete set aan eigentoestanden van de echte HF hamiltoniaan. Deze basis wordt nu gebruikt om de tweede orde Dysonvergelijking zelf-consistent op te lossen, zoals zal worden uitgelegd in het volgende onderdeel.

Tot slot van dit stukje merken we nog op dat de keuze van de parameters van de muur (sterkte $C_l$ en aangrijtingspunt $R_l$) een invloed heeft op de dimensie van de basis set die nodig is opdat de set (bijna) compleet zou zijn. Voor elke waarde van de parameters van de muur geeft het schema dezelfde resultaten als de basis set (bijna) compleet is, maar bij sommige waarden wordt deze (quasi-)compleetheid bereikt bij een kleinere basis dan bij andere waarden. De manier waarop muurparameters en basis set worden geselecteerd komt uitvoerig aan bod in paragraaf 3.5 van hoofdstuk 3 (gesloten schil systemen) en paragraaf 4.2.5 van hoofdstuk 4 (open schil systemen).

### 3.2 Numerieke oplossing van Dyson vergelijking tot op tweede orde in de interactie.

Het oplossen van de Dyson vergelijking tot op tweede orde, het Dyson(2) schema, is heel wat moeilijker dan tot op eerste orde [het Dyson(1) schema].

Zoals vermeld in paragraaf 2, wordt vaak de aannname gedaan dat de Greense functie diagonaal is in de basis voor de configuratierruimte [in oase de HF basis set gegenereerd door het Dyson(1) schema]. Hoewel niet nodig vanuit theoretisch standpunt, wordt deze onderstelling vooral van belang in het Dyson(2) schema omdat het de toch al zware numerieke belasting sterk reduceert. Door deze diagonale benadering kan de Greense functie uit vergelijking (7) binnen de discrete HF basis set geschreven worden als een som van enkelvoudige polen

$$ G_a(E) = \sum_j \frac{S^f_{a,j}}{E - \epsilon^f_{a,j} + i\eta} + \sum_j \frac{S^b_{a,j}}{E - \epsilon^b_{a,j} - i\eta}, $$

waar de sommatieindex $j$ wordt beperkt tot de toestanden van het $(A \pm 1)$-elektronen systeem die kunnen worden bereikt vanuit de gesloten schillen configuratie door een elektron bij te creëren of te verwijderen in orbitaal $a$. Ook hebben we volgende verkorte notatie ingevoerd $\epsilon^f_{a,j} = E_{j,A+1} - E_{0,A}$ en $\epsilon^b_{a,j} = E_{0,A} - E_{j,A-1}$ voor respectievelijk de voorwaartse en de achterwaartse energieën. Het is verder nuttig te vermelden dat bij het toepassen van de HF basis in vergelijking (7), $a$ staat voor een set van vier kwantumgetallen:

$$ a = (n_a, l_a, m_{l_a}, m_{s_a}), \quad (24) $$

terwijl $a$ in vergelijking (23) slechts uit een subset bestaat: $a = (n_a, l_a)$. Zo geldt
dat
\[ G_a(E) = \frac{1}{2(2l_a + 1)} \sum_{m_{a,n}} G_\alpha(a,E). \] (25)

We herinneren eraan dat de eerste term in vergelijking (23) behoort bij het zogenaamde voorwaarts in de tijd propagerende deel en excitaties beschrijft in het \((A+1)\)-elektronen systeem, terwijl de tweede term (achterwaarts in de tijd propagerend) excitaties beschrijft in het \((A-1)\)-elektronen systeem.

De tweede orde zelf-energie van vergelijking (16) wordt
\[ \Sigma_a^{(2)}(E) = \sum_{b,c,d} \frac{F_{ab,c,d}}{4(2l_a + 1)} \sum_{j,k,l} \left\{ \frac{S_{l,j}^f S_{d,k}^f S_{b,l}^b}{E - \left( \epsilon_{u,j}^f + \epsilon_{v,k}^f - \epsilon_{w,l}^b \right) + i\eta} + \frac{S_{l,j}^b S_{d,k}^b S_{b,l}^f}{E - \left( \epsilon_{u,j}^b + \epsilon_{v,k}^b - \epsilon_{w,l}^f \right) - i\eta} \right\}, \] (26)

waarin
\[ F_{ab,c,d} = \sum_{LS} (2L + 1)(2S + 1) | \langle ab | LS \rangle \langle W | (cd)LS \rangle_{ab} |^2. \] (27)

Zoals eerder vermeld, is de diagonale vorm van de tweede orde Greense functie te schrijven als [zie ook vergelijking (17)]
\[ G_a^{(2)}(E) = \frac{1}{E - \epsilon_{HF} - \Sigma_a^{(2)}(E)}. \] (28)

Voor de self-consistente oplossing van Dysons vergelijking gebruiken we volgend iteratief schema. In eerste iteratie wordt de Greense functie van vergelijking (23) geinitialiseerd met de HF benadering
\[ G_a^{(2)[1]}(E) = \frac{\theta \left( \epsilon_{HF} - \epsilon_{a} \right)}{E - \epsilon_{HF} + i\eta} + \frac{\theta \left( \epsilon_{F} - \epsilon_{HF} \right)}{E - \epsilon_{HF} - i\eta}. \] (29)

Door middel van vergelijking (26) kan de tweede orde zelf-energie in eerste iteratie, \( \Sigma_a^{(2)[1]}(E) \), gevonden worden.

In het algemeen kan de tweede orde zelf-energie in iteratie \( n \), \( \Sigma_a^{(2)[n]}(E) \), berekend worden m.b.v. vergelijking (26) en de \( n \)de iteratie Greense functie \( G_a^{(2)[n]}(E) \). De Greense functie \( G_a^{(2)[n+1]}(E) \) van de volgende iteratie wordt dan gegeven door
\[ G_a^{(2)[n+1]}(E) = \frac{1}{E - \epsilon_{HF}^n - \Sigma_a^{(2)[n]}(E)}, \quad n = 1, 2, \ldots \] (30)
Om $G_a^{(2)[n+1]}$ in de vorm van vergelijking (23) te brengen, dienen de polen $e_{a,j}^{[n+1]}$ van $G_a^{(2)[n+1]}$ te worden bepaald. Deze zijn de oplossingen van

$$
e_{a,j}^{[n+1]} = e_a^{HF} + \Sigma_a^{(2) [n]} (e_{a,j}^{[n+1]}),$$

en de corresponderende residu's $S_{a,j}^{[n+1]}$ (de spectroscopische sterkte van de pool van de Greeense functie) worden dan uiteraard gegeven door

$$S_{a,j}^{[n+1]} = \left( 1 - \frac{1}{E - e_{a,j}^{[n+1]}} \right) \frac{d}{dE} \Sigma_a^{(2) [n]} (E).$$

Aangezien de zelf-energie afhangt van de Greeense functie, hangt ook het gemiddeld veld $\Sigma^{(1)}$ af van de uiteindelijke (d.w.z. tweede orde) Greeense functie. Daarom worden na iedere iteratie de ééndeelejesenergieën $e_a^{HF}$ opnieuw geëvalueerd om de veranderingen in de bezetting van alle ééndeelejorbitalen in rekening te brengen

$$e_a^{HF} = \langle a | H_0 | a \rangle + \sum_{c,L,S} \langle (ac)LS | W | (ac)LS \rangle a \sum_j S_{c,j}^{[n]}.$$

Bovenstaand algoritme wordt herhaald tot convergentie is bereikt (de Greeense functie van een bepaalde iteratie wijzigt niet meer t.o.v. die van de vorige iteratie). Een diagrammatisch overzicht van de Dyson vergelijking wordt gegeven in Fig. 3, waar ook vergelijking (33) wordt in rekening gebracht.

### 3.3 Het BAGEL schema.

Het grootste probleem bij het oplossen van de Dyson vergelijking tot op tweede orde in de interactie is de grote toename in het aantal polen van de Greeense functie en de zelf-energie tijdens de iteraties. Deze toename kan worden afgeleid uit vergelijking (26); we zien dat $D$ polen voor de Greeense functie van iteratie $n$ ongeveer $D^2$ polen zullen genereren in de zelf-energie van iteratie $n$, wat ook ongeveer het aantal polen zal zijn voor de Greeense functie van iteratie $n + 1$. We zien dat het aantal polen drastisch toeneemt, en bijgevolg snel onhandelbaar wordt.

Om dit probleem te omzeilen bestaan verschillende methodes. In dit werk wordt het BAGEL (BAasis GEnerated by Lanczos) algoritme aangewend, waarvan we hier kort de gedachten gang schetsen. Een uitvoeriger uiteenzetting kan worden gevonden in hoofdstuk 3.

Algemeen wordt het probleem waarvoor het BAGEL schema een antwoord biedt als volgt gesteld. De tweede orde zelf-energie in vergelijking (26) kan in een compactere gedaante worden omgevormd

$$\Sigma_a^{(2)} (E) = \sum_{j=1}^{D^2} \frac{\sigma_j^f}{E - \omega_j^f + i\eta} + \sum_{j=1}^{D^b} \frac{\sigma_j^b}{E - \omega_j^b - i\eta},$$

waarbij $D^f$ en $D^b$ de dimensies van de fictieve en de bond orbitale zijn.
Samenvatting. *Ab initio* studie van Dichtheidsfunctionaaltheorie via Greense functies.

![Diagram](image)

Figuur 3: Diagrammatische representatie van de tweede orde Dyson vergelijking.

en omvat een groot aantal \((D^f + D^b)\) enkelvoudige polen. In het zogenaamde BAGEL\((M,M)\) schema wordt deze som vervangen door een som met een veel kleinere dimensie \(M\),

\[
\Sigma^{(2)}_{\alpha}(E) = \sum_{j=1}^{M} \frac{\tilde{\sigma}^f_j}{E - \tilde{\omega}^f_j + i\eta} + \sum_{j=1}^{M} \frac{\tilde{\sigma}^b_j}{E - \tilde{\omega}^b_j - i\eta}. \tag{35}
\]

De nieuwe polen op posities \(\tilde{\omega}^f_j, \tilde{\omega}^b_j\) en met residu’s \(\tilde{\sigma}^f_j, \tilde{\sigma}^b_j\) worden bepaald zodat de laagste \(2M\) energiegewogen momenten van de distributie van de zelf-energie worden gereproduceerd. Dit betekent dat voor \(p = 0, 1, \ldots, 2M - 1\),

\[
\mu^{f}_{\alpha}(p) \ = \ \sum_{j=1}^{D^f} \sigma^f_j \left(\omega^f_j\right)^p = \sum_{j=1}^{M} \tilde{\sigma}^f_j \left(\tilde{\omega}^f_j\right)^p \tag{36}
\]

\[
\mu^{b}_{\alpha}(p) \ = \ \sum_{j=1}^{D^b} \sigma^b_j \left(\omega^b_j\right)^p = \sum_{j=1}^{M} \tilde{\sigma}^b_j \left(\tilde{\omega}^b_j\right)^p. \tag{37}
\]

Bij het oplossen van de Dyson vergelijking, wordt de volledige zelf-energie \(\Sigma^{(2)}_{\alpha}(E)\) vervangen door de BAGEL\((M,M)\) benadering \(\tilde{\Sigma}^{(2)}_{\alpha}(E)\). Het is duidelijk dat als \(M\) klein wordt gekozen (orde 20), de BAGEL Greense functie een kleiner aantal polen zal hebben dan de echte Greense functie \((2M + 1)\) in totaal) en dat de dimensionaliteit over de achtereenvolgende iteraties vast blijft.
De voorwaarden (36-37) op de momenten van de BAGEL zelf-energie $\Sigma^{(2)}$ beperken ook de distributie van de spectroscopische sterkte van de corresponderende BAGEL Greense functie: er kan worden aangetoond dat zijn energie-gewogen momenten van orde $p = 0, 1, \ldots, 2M + 1$ gelijk zijn aan deze van de Greense functie die is bekomen met de originele zelf-energie $\Sigma_0^{(2)}(E)$ (zie hoofdstuk 3). Samenvattend kunnen we stellen dat de BAGEL(M,M) benadering de eerste $2M$ orde momenten van het achterwaartse en voorwaartse deel van de zelf-energie afzonderlijk reproduceert [zie vergelijkingen (36) en (37)] en de eerste $2M + 2$ orde momenten van de *totale* Greense functie. Voor de atomaire systemen in dit werk waren 20 tot 25 BAGEL polen voldoende voor een goede beschrijving van de spreiding van de spectroscopische sterkte die wordt veroorzaakt door de correlaties in het Dyson(2) schema.

### 3.4 Resultaten voor gesloten schil atomen.

In dit onderdeel bespreken we enkele resultaten van de berekeningen op de gesloten schil atomen He, Be, Ne, Mg, Ar en Kr. Dit laatste atoom werd in rekening gebracht om na te gaan hoezeer relativistische correcties [niet opgenomen in het Dyson(2) schema] een impact hebben voor zware atomen (zie ook [75], [76]). Waar mogelijk wordt een experiment getoetst. Ook vergelijken we de Dyson(1) en Dyson(2) resultaten met andere veevelektjesberekeningen op standaard HF, post-HF en Dichtheidsfunctionaaltheorie (DFT) niveau. Deze berekeningen werden met het GAUSSIAN 98 pakket [77] berekend en voor details omtrent deze numerieke schema’s verwijzen we b.v. naar [12]. De GAUSSIAN 98 berekeningen worden alle in een eindige basis berekend en daarom is vergelijking met de resultaten van dit werk (bekomen in een quasi-complete basis) niet helemaal gerechtvaardigd. We vermelden de GAUSSIAN 98 resultaten enkel om een idee te geven wat het effect is van de correlaties die in het Dyson(2) schema op zelf-consistente manier worden ingebouwd. Zoals zal blijken uit de resultaten, genereren de correlaties een (substantiële) shift t.o.v. de Dyson(1) voorspelling naar het experiment toe.

Allereerst bekijken we de invloed van de correlaties op de spectrale functie. In het Dyson(1) schema heeft deze volgende gedaante

$$S_\alpha(E) = S_\alpha^p(E) + S_\alpha^h(E),$$

waarbij de deeltje spectrale functie [vergelijking (8)] en de gat spectrale functie [vergelijking (9)] werden gebruikt.

In Fig. 4 tonen we de spectrale functie voor de $2p$ orbital in Ne voor het Dyson(1) schema en in het Dyson(2) schema na één iteratie en na convergentie. We zien dat op HF niveau alle sterkte in één pick geconcentreerd is die zich situeert op de HF ééndeeltjesenergie. Uit Fig. 4 maken we ook op dat in de eerste iteratie van het Dyson(2) schema een depletie van de sterkte van de HF pick optreedt. Door de energie-afhankelijkheid van de zelf-energie (de correlaties in het tweede orde schema)
wordt de overblijvende sterkte verdeeld over andere energetieen. Het effect van de zelf-consistentie is dat de sterkte van de vele satellietpolen van de eerste iteratie wordt gegroepeerd in een klein aantal polen met een grotere sterkte. De energie van de sterkste pool blijft hierbij nagenoeg ongewijzigd.

Figuur 4: Spectrale functie van de 2p orbitaal in Ne op HF [Dyson(1)] en Dyson(2) niveau (atomaire eenheden).

In Tabel 1 vermelden we de eerste ionisatie energieën zoals voorspeld door verschillende schema's. We zien dat de voorspellingen voor de ionisatie energie door het DFT schema niet goed zijn. Dit komt doordat de ionisatie energie is berekend a.h.v. de hoogst bezette orbitaal en niet door het verschil te nemen tussen de grondtoe-
stand van het atoom en het ion. In dit laatste geval zouden de DFT resultaten veel beter zijn. We zien dat de HF ionisatie energieën van GAUSSIAN 98 (derde kolom) en Dyson(1) (vierde kolom) goed overeenkomen, al zijn er soms grote verschillen met het experiment. Het is daarom ook opvallend dat de correcties in de eerste iteratie van het Dyson(2) schema al van die aard zijn dat een goede overeenkomst met het experiment bijna is bereikt. We zien ook dat de correlaties in de eerste iteratie van het tweede orde schema overschat worden voor Be en Mg: de evolutie naar convergentie oscilleert. Voor krypton is het duidelijk dat het Dyson(2) schema invloeden zoals screening (hogere orde diagrammen) en relativistische effecten mist om een goede overeenkomst met het experiment te verkrijgen.

Gelijkwaardige conclusies kunnen worden getrokken voor de totale bindingsenergie.
Tabel 1: Eerste ionisatie energie voor enkele atomen (atomaire eenheden). Dyson(1)
staat voor de voorspelling op HF niveau, Dyson(2) geeft de resultaten van het tweede
orde schema na één iteratie, twee iteraties en na convergentie.

<table>
<thead>
<tr>
<th></th>
<th>DFT-BLYP</th>
<th>DFT-BLYP</th>
<th>HF/6-31+g**</th>
<th>Dyson(1) eerste it.</th>
<th>Dyson(1) tweede it.</th>
<th>Dyson(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.578</td>
<td>0.659</td>
<td>0.517</td>
<td>0.518</td>
<td>0.506</td>
<td>0.506</td>
</tr>
<tr>
<td>Ne</td>
<td>0.460</td>
<td>0.560</td>
<td>0.342</td>
<td>0.350</td>
<td>0.340</td>
<td>0.340</td>
</tr>
<tr>
<td>Mg</td>
<td>0.158</td>
<td>0.184</td>
<td>0.233</td>
<td>0.233</td>
<td>0.237</td>
<td>0.237</td>
</tr>
<tr>
<td>Ar</td>
<td>0.270</td>
<td>0.427</td>
<td>0.590</td>
<td>0.590</td>
<td>0.578</td>
<td>0.578</td>
</tr>
<tr>
<td>Kr</td>
<td>0.333</td>
<td>0.385</td>
<td>0.324</td>
<td>0.324</td>
<td>0.320</td>
<td>0.320</td>
</tr>
</tbody>
</table>

De verwachtingswaarde van de hamiltoniaan (een tweedeeljesoperator) kan worden
berekend met behulp van de ééndeeltje Greense functie aan de hand van de Koltun
somregel ([83], [84]). Deze uitdrukking wordt ook wel de formule van Galtski-
Migdal [85] genoemd. In een vorm waarin de BAGEL polen expliciet optreden,
bekomen we

\[ E_{0(A)} = \frac{1}{2} \sum_{a=1}^{N_b} \sum_{j=1}^{N} \left[ \langle a | H_0 | a \rangle + \epsilon_{a,j} \right] S_{a,j}^{(b)}, \]  

waarin \( N_b \) de dimensie is van de HF basis set, \( N \) het aantal (achterwaartse) BAGEL
polen en \( H_0 \) het ééndeeltjesstuk (kinetische energie en extern veld) aanduidt van de
hamiltoniaan.

De numerieke resultaten gegeneerd door Dyson(1) en Dyson(2) voor de atomen
in deze studie worden vermeld in Tabel 2. Ook geven we de voorspellingen voor de
HF grondtoestandsenergie wanneer de gelokaliseerde Gaussische basis set HF/6-
311g** wordt gebruikt. De Dyson(1) voorspelling is duidelijk de limiet van de HF
resultaten bekomen in een eindige basis. Perturbatieve methodes zoals de MP
reeksincorporeren gradueel meer correlaties en bekomen steeds betere overeenkomst
met het experiment. De configuratie-interactie (CI) methode vormt theoretisch de
limiet voor deze klasse van post-HF perturbatieve schema’s. Het is duidelijk dat
de resultaten van het Dyson(2) schema superieur zijn aan voornoemde schema’s in
het voorspellen van de totale bindingsenergie. Enkel DFT is competitief met het
Dyson(2) schema, maar dit komt doordat de gebruikte functionalen gefit zijn aan
experimentele energetische data en dus niet echt behoren tot een volledig ab initio
schema (zie [89] en [90] voor de BLYP functionaal en [91] voor de B3LYP functionaal
of zie hoofdstuk 5 van dit werk).

Als besluit kunnen we stellen dat de overeenkomst tussen Dyson(2) en het exper-
iment verrassend goed is. Alleen een klein deel van de totale grondtoestandsenergie
is geïmplementeerd in het Dyson(2) schema, wat te wijten kan zijn aan de dia-
gonale benadering voor de Greense functie en de zelf-energie of aan hogere orde (en
relativistische) effecten die niet in het schema zijn opgenomen.
Tabel 2: Totale grondtoestandsenergie voorspeld door verschillende veeldeeltjesmodellen (ataomaire eenheden).

<table>
<thead>
<tr>
<th></th>
<th>DFT-BLYP</th>
<th>DFT-B3LYP</th>
<th>HF/6-311g**</th>
<th>Dyson(1)</th>
<th>Post-HF</th>
<th>CI</th>
<th>Dyson(2)</th>
<th>Expt. [88]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>Be</td>
<td>Ne</td>
<td>Mg</td>
<td>Ar</td>
<td>Kr</td>
<td>eerste it.</td>
<td>-2.904</td>
</tr>
<tr>
<td>DFT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>tweede it.</td>
<td>-2.899</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>conv.</td>
<td>-2.899</td>
</tr>
<tr>
<td>Dyson(1)</td>
<td>-2.860</td>
<td>-14.572</td>
<td>-128.523</td>
<td>-199.607</td>
<td>-536.807</td>
<td>-2751.962</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP3</td>
<td>-2.899</td>
<td>-14.609</td>
<td>-128.731</td>
<td>-199.636</td>
<td>-536.966</td>
<td>-2752.106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP4(DQ)</td>
<td>-2.890</td>
<td>-14.613</td>
<td>-128.733</td>
<td>-199.638</td>
<td>-536.966</td>
<td>-2752.105</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MP4(SDTQ)</td>
<td>-2.890</td>
<td>-14.613</td>
<td>-128.733</td>
<td>-199.638</td>
<td>-536.966</td>
<td>-2752.107</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Voor een bespreking van andere observabelen die kunnen worden voorspeld met het Dyson (1) en Dyson (2) schema, zoals eéndehetjesenergieën en -sterktes, verwijzen we naar hoofdstuk 3.

4 Zelf-consistente oplossing van Dysons vergelijking voor open schil atomen.

In deze paragraaf zullen we de uitbreiding bespreken van het algoritme om de Dyson vergelijking zelf-consistent tot op tweede orde op te lossen voor open schil atomen. We geven hier slechts een overzicht, een volledige uiteenzetting kan worden gevonden in hoofdstuk 4. Bij de bespreking van deze atomen wordt een nieuwe grootheid van belang, nl. de elektronenaﬃniteit. Vooral voor deze observabele zullen de correlaties in het Dyson (2) schema onmisbaar blijken om een goede overeenkomst met het experiment te bereiken.

4.1 Veralgemeen formalisme en numeriek schema voor open schil atomen.

In deze uitbreiding bekijken we open schil atomen uit de tweede rij van het periodiek systeem (B, C, N, O en F), waarbij de 2p orbitaal maar gedeeltelijk bezet is. Het
probleem bij open schil atomen is dat we bij sommaties over de bezette $m_l$ kwantumgetallen in een bepaalde $(n,l)$ orbitaal niet meer het volledige bereik hebben. Daarom worden de golffuncties en de ééndeltjesenergieën ook afhankelijk van het $m_l$ kwantumgetal. Hetzelfde geldt voor de spinprojectie $m_s$.

In het algemeen kunnen we de ééndeltjesgolffunctie schrijven als

$$
\varphi_\alpha(r, s) = \frac{1}{r} P_\alpha(r) \ Y_{s,m_a}(\Omega) \ \chi_{m_a}(s),
$$

$$
= \phi_\alpha(r) \ Y_{s,m_a}(\Omega) \ \chi_{m_a}(s). \quad (40)
$$

Hierbij staat $\alpha$ voor $\alpha = (n, l, m_l, m_s)$. In het open schil geval kunnen we de HF vergelijkingen in de volgende vorm brengen

$$
\left( \frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} - \frac{Z}{r} - \epsilon_{HF} \right) P_\alpha(r) + \sum_{\beta(o.o.)} \int dr' D_{\alpha\beta}(r, r') P_\beta(r')^2 \ P_\alpha(r)
$$

$$
- \sum_{\beta(o.o.)} \delta_{m_a m_{a'}} \int dr' E_{\alpha\beta}(r, r') P_{\beta}(r') \ P_\alpha(r') = 0. \quad (41)
$$

De sommatie over $\beta$ beslaat enkel de orbitalen die bezet zijn in de HF grondtoestand. De directe Coulombrepulsie en de uitwisselingsbijdrage tot de HF potentiaal zijn

$$
D_{\alpha\beta}(r, r') = \sum_{LM} \frac{4\pi}{2L+1} \langle l_m \ Y_L | l_m' \ Y_L' \ | l_m \ Y_L \rangle \langle l_m' Y_L | l_m' Y_L' \ | l_m' \ Y_L' \rangle
$$

$$
E_{\alpha\beta}(r, r') = \sum_{LM} \frac{4\pi}{2L+1} \langle l_m \ Y_L | l_m' \ Y_L' \ | l_m \ Y_L \rangle \langle l_m Y_L' | l_m' Y_L' \ | l_m' \ Y_L' \rangle,
$$

waar

$$
\langle l_m Y_L | l_m' Y_L' \rangle = \int d\Omega \ Y^{*}_L m_a(\Omega) \ Y_L(\Omega) Y_{s,m_a}(\Omega). \quad (43)
$$

Als we in het Dyson(2) schema de volledige set aan kwantumgetallen zouden moeten meenemen, zouden de berekeningen onaanvaardbaar lang duren. Daarom wordt voor B, C, O en F een uitmiddelingsprocedure over het $m_l$ kwantumgetal uitgevoerd. Voor stikstof is geen uitmiddeling nodig, aangezien we veronderstellen dat in dit atoom alle 2p-electronen één enkele spinprojectie hebben (conform met de regel van Hund die stelt dat de elektronen een grondtoestandsconfiguratie verkiesen met een maximale spinmultipliciteit, zie b.v. [12]). We lichten nu de uitmiddelingsmethode wat nader toe.

Als $l \neq 1$ zijn de orbitalen of volledig bezet of volledig onbezet. De sferische uitmiddeling komt dan neer op het sommeren over alle subtoestanden $m_l$ in vergelijking (42) en het delen door de ontaarding $2l + 1$. Deze orbitalen worden beschreven door de radiale golffuncties $P_\alpha(r)$ die worden gekarakteriseerd door de kwantumgetallen $a = (n, l, m_s)$, onafhankelijk van $m_l$.

Voor de $l = 1$ orbitalen moet de uitmiddeling zo worden uitgevoerd dat er geen zelf-interactie in het HF gemiddeld veld optreedt voor de bezette $2p$ toestanden. We
beperken de representatie van de $l = 1$ spinruimte (die normaal drie componenten heeft) tot twee types van radiale golffuncties: één geassocieerd met de bezette $2p m_s$ subruimte (aangeduid met $\kappa = 1$) en één geassocieerd met de onbezette $2p m_s$ subruimte (aangeduid met $\kappa = 0$). Op die manier kunnen we de $l = 1$ spin orbitalen karakteriseren d.m.v. de kwantumgetallen $a = (n_a, l_a = 1, m_s, \kappa_a)$, onafhankelijk van $m_l$. De correspondende ontaarding $d_a$ hangt af van de bezettingsgraad $n_p$ van de $2p$ spin orbital met één of twee elektronen: $n_p = 1$ voor de B en O atomen en $n_p = 2$ voor C en F. Voor $l_a = 1$ hebben we dus dat $d_a = n_p$ voor $\kappa_a = 1$ en $d_a = 3 - n_p$ voor $\kappa_a = 0$. Om dit wat duidelijker te maken is het labelschema gevisualiseerd in Fig. 5. Merk op dat omwille van orthogonaliteitsredenen, deze uitmiddeling moet worden doorgevoerd voor alle $l = 1$ orbitalen, niet alleen de $2p$.

![Diagram](image_url)

**Figuur 5:** Gedeeltelijk gevulde $2p$ spin orbital voor de open schil atomen B, C, O en F. Voor B en C onderstellen we de spin-down orbitala gedeeltelijk bezet terwijl de spin-up volledig onbezet is. Voor O en F is de spin-down volledig bezet, terwijl de spin-up gedeeltelijk bezet is. Voor de duidelijkheid zijn alleen de gevallen voor O en F voorgesteld (spin-up polarisatie van de pijltjes). Zoals in de tekst, staat $n_p$ voor het aantal elektronen in de gedeeltelijk bezette spin orbitala en staat $d$ voor de ontaarding van de orbitala gekarakteriseerd door de kwantumgetallen $(n, l, m_s, \kappa)$. 
De uit middelingsprocedure leidt tot volgende uitgemiddelde HF potentiaal:

\[
\tilde{D}_{ab}(r, r') = \frac{1}{3} \sum_{\mu} \frac{1}{d_a d_b} \sum_{m_{l_a} m_{l_b}} w_{\alpha \mu} w_{\beta \mu} D_{\alpha \beta}(r, r'), \\
\tilde{E}_{ab}(r, r') = \frac{1}{3} \sum_{\mu} \frac{1}{d_a d_b} \sum_{m_{l_a} m_{l_b}} w_{\alpha \mu} w_{\beta \mu} E_{\alpha \beta}(r, r'),
\]

waar de sommatie over \( m_{l_a} \) en \( m_{l_b} \) wordt beperkt door de \( w_{\alpha \mu} \) en \( w_{\beta \mu} \) coëfficiënten volgens

\[
\begin{cases} 
  l_a \neq 1 : w_{\alpha \mu} = 1 \\
  l_a = 1, \ d_a = 2 : w_{\alpha \mu} = 1 - \delta_{m_{l_a} \mu} \\
  l_a = 1, \ d_a = 1 : w_{\alpha \mu} = \delta_{m_{l_a} \mu}.
\end{cases}
\]

In vergelijking (44) duidt de factor \( 1/3 \) en de sommatie over \( \mu = -1, 0, 1 \) de uit middel ing aan over de \( m_l \) waarden in de \( np \) \( m_s \) spin orbitaal. De coëfficiënten \( w_{\alpha \mu} \) in vergelijking (45) selecteren automatisch de correcte \( m_l \) waarden voor iedere keuze van \( \mu \).

De uiteindelijke HF vergelijkingen in de coördinatenruimte (voor zowel bezette als onbezette toestanden) zijn dan

\[
\left( -\frac{1}{2} \frac{d^2}{dr^2} - \frac{l_a(l_a + 1)}{r^2} - \frac{Z}{r} - e_{lF}^F \right) P_a(r) + \sum_{b(occ.)} d_b \int dr' \tilde{D}_{ab}(r, r') P_b(r')^2 P_a(r) - \sum_{b(occ.)} d_b \delta_{m_{l_a} m_{l_b}} \int dr' \tilde{E}_{ab}(r, r') P_b(r') P_a(r') P_b(r) = 0.
\]

Samenvattend stellen we dat in het uit middelingschema de spinvrijheidsgraad ongemoeid wordt gelaten: de uit middelingsprocedure gaat enkel over \( m_l \). Voor \( m_s = \pm \frac{1}{2} \) geeft deze procedure één enkele HF hamiltoniaan in geval \( l \neq 1 \) en twee HF hamiltonianen corresponderend met \( \kappa = 0 \) en \( \kappa = 1 \) in de \( l = 1 \) geval. De constructie van een complete en orthonormale set aan ééndeeltjesorbitalen kan dan eenvoudig gebeuren. Vergeleken met het gesloten schil geval in vorige paragraaf, wordt het aantal orbitalen in de (bijna) complete set meer dan verdubbeld, waardoor de numerieke belasting ook sterk toeneemt. Daarom werd het programma voor het open schil probleem geïmplementeerd in een parallelle (twee draadige) code, waarbij optimaal kan worden gebruikgemaakt van de hedendaagse computerarchitectuur.

Eens de HF basis set is geconstrueerd, kan het Dyson(2) schema worden toegepast. Dit algoritme is sterk gelijkend aan dat van de gesloten schil atomen, besproken in onderdeel 3.2. Een volledig overzicht van het Dyson(2) algoritme voor open schil systemen kan worden gevonden in hoofdstuk 4. Hier vermelden we enkel dat vergelij-
king (26) moet worden vervangen door

\[
\Sigma_a^{(2)}(E) = \sum_{b,c,d} \frac{F_{a,b}^{cd}}{2d_a} \sum_{j,k,l} \left\{ \frac{S_{c,j}^f S_{d,k}^f S_{b,l}^b}{E - (\epsilon_{c,j}^f + \epsilon_{d,k}^f - \epsilon_{b,l}^b) + i\eta} + \frac{S_{b,l}^b S_{d,k}^f S_{c,j}^f}{E - (\epsilon_{c,j}^f + \epsilon_{d,k}^f - \epsilon_{b,l}^b) - i\eta} \right\}
\]

(47)

De coëfficiënten \(F_{a,b}^{cd}\) worden als volgt bepaald (hierbij is \(W\) de Coulomb interactie)

\[
F_{a,b}^{cd} = \frac{1}{3} \sum_{\mu} \sum_{m_{i,a},m_{i,b},m_{i,c},m_{i,d}} w_{\mu m_{i,a}} w_{\mu m_{i,b}} w_{\mu m_{i,c}} w_{\mu m_{i,d}} \langle (am_{i,a})(bm_{i,b}) | W | (cm_{i,c})(dm_{i,d}) \rangle_{a\beta} \right|^2,
\]

waarbij de sommatie over \(\mu = -1, 0, 1\) de uitkomst van de \(m_l\) waarden in de \(np m_s\) spin orbitaal. Ook vergelijking (33) moet worden vervangen door

\[
e_a^{HF[n]} = \langle a | H_0 | a \rangle + \frac{1}{d_a} \frac{1}{3} \sum_{\mu} \sum_{m_{i,a},m_{i,c}} w_{\mu m_{i,a}} w_{\mu m_{i,c}} \langle (am_{i,a})(cm_{i,c}) | W | (am_{i,a})(cm_{i,c}) \rangle_{a\alpha} \sum_j S_{c,j}^b[n],
\]

(49)

4.2 Resultaten voor open schil atomen.

In dit onderdeel behandelen we de belangrijkste resultaten van het Dyson(1) en Dyson(2) schema voor de atomen B, C, N, O en F. Ook vergelijken we net als in het gesloten schil geval met het experiment en met andere rekenschema's. Zoals steeds worden alle resultaten in atomaire eenheden uitgedrukt.

In Tabel 3 en 4 geven we de voorspellingen voor de eerste ionisatie energie en voor de elektronenaanfinititeit. Deze grootheden kunnen op twee manieren worden berekend. Ondertussen maakt men een aparte optimalisatie van ion en atoom en worden de totale energieën afgetrokken (adiabatische werkweg), ofwel neemt men de energie van de hoogst bezette (laagste onbezette voor de elektronenaanfinititeit) orbitaal en wordt het ten einde gebracht. Aangezien de Greense functie excitaties in het \(A \pm 1\) systeem beschrijft uitgaande van het \(A\) elektronen systeem, behoren de Dyson(1) en Dyson(2) resultaten tot de tweede categorie. In de tabellen worden voorbeelden van beide categorieën gegeven.

In Tabel 3 zien we dat de DFT resultaten het best zijn bij een adiabatische aanpak. Voor de HF schema's zien we dat Dyson(1) in de lijn van de andere resultaten ligt en een goede start geeft voor het Dyson(2) schema. De correlatie effecten die in dit schema geïncludeerd worden hebben duidelijk een gunstig effect op de resultaten.

In Tabel 4 worden de resultaten voor de elektronenaanfinititeit toegend. Het is welbekend in de wetenschappelijke gemeenschap dat deze grootheid één van de moeilijkst te reageren observabelen is in een \textit{ab initio} berekening. Zo zien we b.v. uit
Tabel 3: Eerste ionisatie energieën in atomaire eenheden. Dyson(1) staat voor HF in de discreet basis zoals vermeld in de tekst. Dyson(2) omvat de oplossing van de tweede orde Dyson vergelijking na één iteratie, na twee iteraties en na convergentie. Experimentele data werden gehaald uit Ref. [110] (\textsuperscript{a}), Ref. [111] (\textsuperscript{b}), Ref. [112] (\textsuperscript{c}), Ref. [113] (\textsuperscript{d}) en Ref. [114] (\textsuperscript{e}).

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>Dyson(2)</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.317</td>
<td>0.317</td>
<td>0.308</td>
</tr>
<tr>
<td>C</td>
<td>0.417</td>
<td>0.417</td>
<td>0.410</td>
</tr>
<tr>
<td>N</td>
<td>0.532</td>
<td>0.534</td>
<td>0.535</td>
</tr>
<tr>
<td>O</td>
<td>0.545</td>
<td>0.547</td>
<td>0.516</td>
</tr>
<tr>
<td>F</td>
<td>0.643</td>
<td>0.647</td>
<td>0.672</td>
</tr>
</tbody>
</table>

De Dyson(1) berekening dat de resultaten zeker niet goed zijn; in een HF beschrijving zou geen enkel atoom een negatief ion kunnen vormen. Bijgevolg zijn de Dyson(1) resultaten geen goede start voor het Dyson(2) schema, in tegenstelling tot het geval voor de ionisatie energie. Het is daarom ook verrassend dat het Dyson(2) schema voor bijna alle atomen al in de eerste iteratie de elektronenaaffiniteit de goede kant op stuurt. De elektronenaaffiniteit is een goede test voor de beschrijvende capaciteit van rekenschema's omdat hier correlaties erg belangrijk zijn. Dit is zeker het geval voor boor, dat het lichtst gebonden stabiele negatief ion vormt onder de open schil atomen die hier zijn beschouwd (zie ook Ref. [115]). We zien dat in dit geval twee iteraties nodig zijn opdat genoeg correlaties in het schema zouden worden ingebouwd om een extra elektron te kunnen binden. We zien ook dat voor stikstof de elektronenaaffiniteit negatief blijft, zelfs na convergentie. Dit wordt bevestigd door het experiment, waar men er nog niet in is geslaagd om een anion voor stikstof te vinden (zie b.v. [125] en [126]). Vooral de voorspelling van fluor is in goede overeenkomst met het experiment, hoewel dit atoom erom bekend staat een affiniteit te hebben die zeer moeilijk te reproduceren is (zie b.v. Refs. [118, 121, 122, 129]). Ter vergelijking geven we ook de resultaten van een coupled-cluster (CCSDT) studie van de elektronenaaffiniteit die gebruik maakt van de adiabatische methode en een groot aantal correcties (zoals relativistische correcties en eindige basis set limit) invoert (Ref. [118]). Bijgevolg kan men de resultaten van Ref. [118] aanzien als een van de meest nauwkeurige op het ogenblik van schrijven van dit werk. Voor een volledig overzicht van de ééndedeljesenergieën verwijzen we naar hoofdstuk 4.

Tot slot includeren we ook nog de resultaten voor de totale energie in Tabel 5. In het Dyson(2) schema werd voor de berekening van de totale energie weer gebruik gemaakt van de formule van Galitskii-Migdal (39), zij het dan aangepast om met het uitmiddelingschema rekening te houden. Ook hier kunnen de conclusies van de gesloten schil resultaten worden doorgetrokken: de Dyson(2) resultaten zijn beter dan de HF en post-HF methodes, maar DFT blijft superieur. Zoals aangeduid in de
Samenvatting. *Ab initio* studie van Dichtheidsfunctionaaltheorie via Greense functies.


<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BLVP</td>
<td>BLVP</td>
<td>cc(11)</td>
<td>cc(11)</td>
<td>cc(11)</td>
</tr>
<tr>
<td>B</td>
<td>-0.005</td>
<td>-0.002</td>
<td>-0.008</td>
<td>-0.0354</td>
<td>-0.009</td>
</tr>
<tr>
<td>C</td>
<td>0.0145</td>
<td>0.0072</td>
<td>0.04641</td>
<td>-0.002</td>
<td>0.0033</td>
</tr>
<tr>
<td>N</td>
<td>0.0478</td>
<td>0.0428</td>
<td>-0.0109</td>
<td>-0.1080</td>
<td>-0.0491</td>
</tr>
<tr>
<td>O</td>
<td>0.0642</td>
<td>0.0077</td>
<td>0.05368</td>
<td>-0.0792</td>
<td>0.014</td>
</tr>
<tr>
<td>P</td>
<td>0.0642</td>
<td>0.0077</td>
<td>0.12505</td>
<td>-0.0369</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Vorige paragraaf is dit succes van DFT voornamelijk te wijten aan de semi-empirisch karakter van de functionalen die in DFT worden gebruikt.

Als besluit kunnen we stellen dat de Dyson(2) berekeningen heel wat correlaties in zich dragen en bijgevolg een accurate beschrijving geven van een veeedeljessysteem. Het grote voordeel van Greense functie berekeningen is dat de correlaties die in het schema worden geïncludeerd, precies kunnen worden geïdentificeerd aan de hand van Feynman diagrammen. Daarom kunnen we via de Greense functie resultaten op zoek gaan naar een microscopische fundering voor functionalen in DFT. In de volgende paragraaf wordt eerst een uiteenzetting gegeven van het DFT formalisme, terwijl we in paragraaf 6 zullen zien hoe de Greense functie berekeningen kunnen worden gebruikt om een *ab initio* basis te genereren voor DFT.

5 Dichtheidsfunctionaaltheorie.

Net als voor het Greense functie formalisme zullen we de theoretische ontwikkeling van Dichtheidsfunctionaaltheorie (DFT) bondig houden en meer aandacht schenken aan de resultaten die eigen zijn aan het onderzoek verbonden aan dit werk. De gedachtengang van het DFT schema werd al in de inleiding van dit hoofdstuk geschept. Daarom gaan we nu onmiddellijk over tot een korte theoretische uiteenzetting van DFT. Een volledigere uiteenzetting kan worden gevonden in hoofdstuk 5.

5.1 De Hohenberg-Kohn theorem's.

De Hohenberg-Kohn theorem's vormen de theoretische grondslag van DFT en tonen aan dat er bij het gebruik van de grondtoestandsdichtheid i.v.m. de golffunctie geen informatie verloren gaat, in tegenstelling tot wat zou worden verwacht op basis van het aantal vrijheidsgraden dat in deze grootheden lijkt ingeboden. De ééndeeltjesdichtheid (kortweg *de* dichtheid) kan als volgt uit de totale *N*-deeltjesgolffunctie
Tabel 5: Totale grondtoestandsenergie (in atomaire eenheden) berekend a.h.v. verschillende veelektjesmodellen. Experimentele data zijn afkomstig van Ref. [88].

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>-24.649</td>
<td>-37.842</td>
<td>-54.583</td>
<td>-75.073</td>
<td>-99.742</td>
</tr>
<tr>
<td>DFT-BLYP</td>
<td>-24.662</td>
<td>-37.856</td>
<td>-54.599</td>
<td>-75.085</td>
<td>-99.754</td>
</tr>
<tr>
<td>HF /6-31g**</td>
<td>-24.529</td>
<td>-37.689</td>
<td>-54.401</td>
<td>-74.809</td>
<td>-99.409</td>
</tr>
<tr>
<td>Dyson (1)</td>
<td>-24.530</td>
<td>-37.690</td>
<td>-54.405</td>
<td>-74.815</td>
<td>-99.412</td>
</tr>
<tr>
<td>MP2</td>
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<td>-37.745</td>
<td>-54.475</td>
<td>-74.918</td>
<td>-99.554</td>
</tr>
<tr>
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<td>-37.760</td>
<td>-54.488</td>
<td>-74.931</td>
<td>-99.563</td>
</tr>
<tr>
<td>CI</td>
<td>QCISD</td>
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<td>-37.766</td>
<td>-54.491</td>
<td>-74.933</td>
</tr>
<tr>
<td>Dyson (2)</td>
<td>eerste it.</td>
<td>-24.585</td>
<td>-37.766</td>
<td>-54.505</td>
<td>-74.944</td>
</tr>
<tr>
<td>tweede it.</td>
<td>-24.597</td>
<td>-37.786</td>
<td>-54.542</td>
<td>-75.008</td>
<td>-99.676</td>
</tr>
<tr>
<td>conv.</td>
<td>-24.600</td>
<td>-37.789</td>
<td>-54.543</td>
<td>-75.010</td>
<td>-99.678</td>
</tr>
<tr>
<td>Expt.</td>
<td>-24.653</td>
<td>-37.844</td>
<td>-54.587</td>
<td>-75.063</td>
<td>-99.725</td>
</tr>
</tbody>
</table>

\[
\Psi(x_1, x_2, \ldots, x_N) \text{ worden bepaald}
\]

\[
\rho(\vec{r}_i) = N \sum_s \int dx_2 \ldots \int dx_N \Psi(x_1, x_2, \ldots, x_N) \Psi^*(x_1, x_2, \ldots, x_N). \quad (50)
\]

Hierbij staat \( x \) voor \((\vec{r}, s)\) (met \( s \) de spinvrijheidsgraad). De dichtheid drukt de totale kans uit om een bepaald elektron te vinden rond het punt \( \vec{r}_i \), onafhankelijk van de plaats van de andere \( N-1 \) electronen.

Het eerste theorema drukt uit dat kennis van de externe potentiaal \( v(\vec{r}_i) \), de totale grondtoestandsgolffunctie \( \Psi_v(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \) en de grondtoestandsdichtheid \( \rho_0(\vec{r}_i) \) volledig equivalent is

\[
v(\vec{r}_1) \Leftrightarrow \Psi_v(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \Leftrightarrow \rho_0(\vec{r}_1), \quad (51)
\]

op voorwaarde dat we weten hoeveel deeltjes zich in het systeem bevinden \((N)\) en dat de tweedelektjesinteractie gespecificeerd is (Coulomb interactie).

Enkele van de relaties in vergelijking (51) kunnen gemakkelijk worden afgeleid. Laat ons een systeem beschouwen met \( N \) elektronen en met de Coulomb interactie als tweedelektjesinteractie \( \hat{W} \). Dan kunnen we een klasse van hamiltonianen definiëren \( \hat{H} = \hat{T} + \hat{V} + \hat{W} \) (\( \hat{T} \) is de kinetische energie operator) door een set \( \mathcal{V} \) van
lokale ééndeeltjespotentialen $\hat{V}$ in te voeren. Elk element van deze set leidt tot een grondtoestand voor het systeem met $N$ fermionen d.m.v. de Schrödingervergelijking

$$\hat{H} | \Psi_v \rangle = E_{gs} | \Psi_v \rangle,$$

waar $E_{gs}$ de grondtoestandsenergie is van het systeem en $| \Psi_v \rangle$ de corresponderende $N$-deeltjesgolffunctie (we beperken ons in deze bespreking tot niet-ontaarde grondtoestanden). We groeperen alle mogelijke grondtoestanden die corresponderen met $\mathcal{V}$ in de set $\Psi$. Het is evident dat de Schrödingervergelijking een relatie vastlegt tussen $\mathcal{V}$ en $\Psi$, namelijk het verband

$$A : \quad \mathcal{V} \Rightarrow \Psi,$$

Dit verband is surjectief: ieder element van $\Psi$ kan worden geassocieerd met minstens één element van $\mathcal{V}$.

Nu beschouwen we de relatie tussen de $N$-deeltjesgolffunctie en de dichtheid (we noteren de verzameling van de dichtheden die we hier beschouwen met $\mathcal{N}$). We groeperen alle mogelijke dichtheden die kunnen worden gegenereerd uit de elementen van $\Psi$ in de verzameling $\mathcal{N}$. Uit de definitie (50) van de dichtheid volgt al dat we ook hier een verband kunnen definiëren

$$B : \quad \Psi \Rightarrow \mathcal{N},$$

dat duidelijk een surjectieve relatie is.

De grote verdienste van het eerste Hohenberg-Kohn theoema is om aan te tonen dat de surjecties $A$ en $B$ eigenlijk bijjecties zijn en dus inverteerbaar [zie vergelijking (51)]. Dit theoema wordt aangetoond via een bewijs uit het ongerijmde en kan worden gevonden in hoofdstuk 5.

De bijzondere relatie tussen de $N$-deeltjesgolffunctie en de ééndeeltjesdichtheid (in de grondtoestand) zorgt ervoor dat alle observabelen $O$ een functionaal worden in de grondtoestandsdichtheid:

$$O[\rho_v] = \langle \Psi[\rho_v] | \hat{O} | \Psi[\rho_v] \rangle,$$

wat de keuze verrechtvaardigt van de elektronendichtheid (in de grondtoestand) als centrale variabele in het formalisme. In het bijzonder wordt ook de totale energie een functionaal in de dichtheid

$$E[\rho_v] = \langle \Psi[\rho_v] | \hat{T} + \hat{W} + \hat{V} | \Psi[\rho_v] \rangle.$$ 

Het Rayleigh-Ritz variationeel principe toont in dit verband volgende eigenschap aan van de functionaal $E[\rho]$:

$$E[\rho_v^0] < E[\rho_v] \quad \text{voor} \quad \rho_v \neq \rho_v^0,$$
waarin $\rho^0$ de niet-ontaarde grondtoestandsdichtheid is die correspondeert met de grondtoestandsenergie $E_{gs} = E[\rho^0] = \min_{\rho\in\mathcal{N}} E[\rho]$.

Zoals hierboven aangegeven, is de ééndeeltjespotentiaal de enige vrijheidsgraad die overblijft voor de hamiltoniaan in Hohenberg-Kohn theorie. Het is daarom interessant de hamiltoniaan te splitsen in een deel dat afhankt van de externe potentiaal en een deel dat universeel is voor alle systemen met een bepaalde tweedeeltjesinteractie:

$$E[\rho_v] = \langle \Psi[\rho_v] | \hat{T} + \hat{W} | \Psi[\rho_v] \rangle + \int d^3r \, v(\vec{r}) \rho_v(\vec{r}) = F_{HK}[\rho_v] + \int d^3r \, v(\vec{r}) \rho_v(\vec{r}).$$  (58)

De functionaal $F_{HK}[\rho_v]$ heeft dezelfde gedaante voor atomen, molecules en vaste stoffen aangezien de tweedeeltjesinteractie $\hat{W}$ in deze gevallen telkens de Coulomb interactie is. Iedere externe invloed (b.v. respectievelijk van één kern, verschillende kernen of het kristalrooster) wordt in de tweede term van vergelijking (58) gestopt. De precieze gedaante van de universele functionaal $F_{HK}[\rho_v]$ is niet gekend en dus moeten benaderingen worden gemaakt om te kunnen rekenen in het DFT schema. De concepten van inverteerbaarheid [vergelijking (51)], de variationele basis [vergelijking (57)] en de universaliteit van $F_{HK}[\rho_v]$ vormen de drie hoekstenen van Hohenberg-Kohn theorie. Bemerk dat er in de theorema’s enkel sprake is van grondtoestandsgrootheden. In dit werk wordt de uitbreiding naar geëxciteerde toestanden niet besproken.

Uitdrukking (57) staat bekend als het tweede theorema van Hohenberg-Kohn: het geeft ons een vergelijking om de grondtoestandsdichtheid te vinden op een directe manier, zonder een toevlucht te moeten zoeken tot de grondtoestandsgolffunctie. We moeten namelijk de energie functionaal (58) minimaliseren met betrekking tot de dichtheid $\rho_v(\vec{r})$ onder de beperking dat $\int d^3r \, \rho_v(\vec{r}) = N$, waar $N$ het aantal deeltjes is (dat vast verondersteld wordt in de theorema’s van Hohenberg en Kohn). Volgens de Lagrange theorie over variatierekening (zie App. D) moet de volgende vergelijking voldaan zijn voor arbitraire variaties van de grondtoestandsdichtheid:

$$\delta \{E[\rho_v] - \mu [\int d^3r \rho_v(\vec{r}) - N] \} = 0,$$  (59)

waarin $\mu$ een Lagrange multiplicator is, die van het gebonden extremum vraagstuk een vrij probleem maakt. Minimalisatie van uitdrukking (59) leidt tot een correct genormeerde grondtoestandsdichtheid. Uit deze uitdrukking leiden we dan de Euler-Lagrange vergelijking af:

$$\frac{\delta E[\rho_v]}{\delta \rho_v(\vec{r})} = \frac{\delta F_{HK}[\rho_v]}{\delta \rho_v(\vec{r})} + v(\vec{r}) = \mu.$$  (60)
Er kan worden aangetoond dat $\mu = \mu(N)$ de chemische potential is van het systeem dat we proberen te bestuderen, d.w.z. $\mu(N) = \frac{\partial E_N}{\partial N}$.

De Hohenberg-Kohn theorie op zich is als eerste goed gefundeerde dichtheidsfunctionaaltheorie op een eerder beperkte schaal toegepast. Op het eerste gezicht is dit verrassend aangezien de numerieke belasting bij het oplossen van de vergelijking (60) in essentie onafhankelijk is van het aantal deeltjes in het systeem. Uiteraard moeten we een benaderende vorm hebben voor de universele functionaal $F_{HK}[\rho_\alpha]$, maar daar zijn uitdrukkingen voor (zie hoofdstuk 5). Er is echter ook een aantal nadenken aan de theorie die moeilijk kunnen worden verholpen binnen het Hohenberg-Kohn schema. Voor de benaderingen van $F_{HK}[\rho_\alpha]$ die gemakkelijk kunnen worden geïmplementeerd, treden problemen op om de asymptotische gebieden in de dichtheid (dicht bij de kern en op eeninde) te beschrijven. Bovendien wordt de typische schilstructuren in de radiale dichtheid [$r^2 \rho_\alpha(r)$] niet teruggevonden en voorspelt de theorie verkeerd eindig het niet bestaan van negatieve ionen en diatomische moleculen. Daarom wordt bij hedendaagse DFT berekeningen een zelf-consistente aanpak verkozen, waarbij de correcte grondtoestandsdichtheid van het interagerend elektronensysteem wordt opgespoord d.m.v. ééndeeltjesorbitalen in een niet-interagerend systeem, gelijkaardig aan de Hartree-Fock methode. Deze praktische manier om DFT berekeningen uit te voeren komt aan bod in het volgende onderdeel.

5.2 Het Kohn-Sham schema.

Zoals vermeld in de vorige paragraaf, is het onmogelijk om een exacte uitdrukking te vinden voor de kinetische energie en de tweedeeltjesinteractie als een directe functionaal in de dichtheid. Daarom ontwierpen Kohn en Sham een schema dat tenminste een groot deel van de kinetische energie exact behandelt. Ze gaan daarbij uit van een niet-interagerend systeem, dat uiteraard exact oplosbaar is aangezien de hamiltoniaan enkel uit ééndeeltjesoperators bestaat

$$\hat{H}_s = \hat{T} + \hat{V}_s.$$  \hspace{1cm} (61)

De Schrödingervergelijking die bij deze hamiltoniaan hoort, is

$$[-\frac{\nabla^2}{2} + v_s(\vec{r})] \phi_\alpha(\vec{r}) = \epsilon_\alpha \phi_\alpha(\vec{r}),$$  \hspace{1cm} (62)

waarbij $\alpha$ zoals gewoonlijk alle kwantumgetallen groepeert die nodig zijn om de ééndeeltjesorbitaal eenduidig te karakteriseren en de golffuncties ge normeerd zijn als $\int d^3 r \phi_\alpha(\vec{r}) \phi_\beta(\vec{r}) = \delta_{\alpha\beta}$. De ééndeeltjesdichtheid van dit niet-interagerend systeem is

$$\rho_s(\vec{r}) = \sum_{\alpha=1}^{N} | \phi_\alpha(\vec{r}) |^2.$$  \hspace{1cm} (63)
Aangezien we nu toegang hebben tot ééndelektrosoorbitalen, kunnen we op eenvoudige en exacte wijze de kinetische energie van het systeem berekenen:

\[ T_s[\rho] = \sum_{\alpha=1}^{N} \int d^3r \, \phi^{*}_\alpha(\vec{r}) \left(-\frac{\nabla^2}{2}\right) \phi_\alpha(\vec{r}). \]  \hfill (64)

Deze functionalis is een *impliciete* functionalis in de dichtheid; de afhankelijkheid gaat enkel via de ééndelektrosoorbitalen (die kunnen worden aanzien als functionalen in dichtheid).

De vaststelling dat de niet-interagerende kinetische energie exact kan worden berekend, lei Kohn en Sham ertoe om een fictief niet-interagerend systeem van deeltjes in te voeren om een interagerend systeem te bestuderen. Het niet-interagerend systeem wordt met het interagerend systeem verbonden door de voorwaarde dat de dichtheid in beide ensembles dezelfde moet zijn: \( \rho(\vec{r}) = \rho_s(\vec{r}) \). Deze conditie wordt gerealiseerd door de externe potentiaal \( v_s(\vec{r}) \) die op het niet-interagerend systeem inwerkt op gepaste wijze te kiezen zodat de niet-interagerende dichtheid in de juiste vorm geknecht wordt.

Om de juiste uitdrukking voor \( v_s(\vec{r}) \) te vinden die de correcte interagerende dichtheid simuleert in het niet-interagerend systeem, vormen we de totale energie van het interagerend systeem om zodat de corresponderende Euler-Lagrange vergelijking de gedaante heeft van een Schrödinger vergelijking voor een niet-interagerend ensemble [zie vergelijking (62)]:

\[
E[\rho] = T[\rho] + \int d^3r \, v(\vec{r}) \rho(\vec{r}) + W[\rho] \\
= F_{HK}[\rho] + \int d^3r \, v(\vec{r}) \rho(\vec{r}) \\
= T_s[\rho] + \int d^3r \, v(\vec{r}) \rho(\vec{r}) + J[\rho] + E_{xc}[\rho],
\]  \hfill (65)

waarbij \( v(\vec{r}) \) de externe potentiaal is die op het interagerend systeem werkt en \( T[\rho] \) en \( W[\rho] \) respectievelijk de kinetische energie en de twee-deeltjesinteractiefunctionaal in het interagerend ensemble voorstellen. Ook hebben we de *directe Coulomb interactie* ingevoerd

\[ J[\rho] = \frac{1}{2} \int d^3r_1 \int d^3r_2 \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} \]  \hfill (66)

en de *uitwisselingscorrelatiefunctionaal*

\[
E_{xc}[\rho] = F_{HK}[\rho] - J[\rho] - T_s[\rho] \\
= T[\rho] - T_s[\rho] + W[\rho] - J[\rho].
\]  \hfill (67)

Het is de bedoeling dat de kinetische energie \( T_s[\rho] \) berekend wordt a.h.v. vergelijking (64). Deze kinetische energie omvat al een groot deel van de kinetische energie van het interagerend systeem zodat \( T[\rho] - T_s[\rho] \) maar een kleine storing voorstelt.
Uiteraard hebben we nu nog de juiste orbitalen nodig om $T_\alpha[\rho]$ mee te evalueren. Deze kunnen worden gevonden door de Euler-Lagrange vergelijking voor de energiefunctieaal (65) op te schrijven en de variaties naar de dichtheid uit te drukken in variaties naar ééndichtheidorbitalen die op een duidige wijze in verband staan met de dichtheid, zoals in vergelijking (63). We hebben dan dat (we onderstellen dat de variaties in $\phi_\alpha$ en $\phi_\alpha^*$ onafhankelijk zijn)

$$
\frac{\delta E[\rho]}{\delta \rho(\vec{r})} \big\vert_{\rho=\rho_0} = \frac{\delta E[\rho]}{\delta \phi_\alpha(\vec{r})} \big\vert_{\phi=\phi_\alpha,\sigma=0} = \frac{\delta E[\rho]}{\delta \phi_\alpha^*(\vec{r})} \big\vert_{\phi=\phi_\alpha^*,\phi_\alpha,\sigma=0} = 0.
$$

(68)

Mits invoeren van Lagrange multiplicatoren $\{e_\alpha\}$ om de orthonormaliteit van de ééndichtheidorbitalen te eisen bekomen we uiteindelijk de Kohn-Sham vergelijkingen

$$
\left[ -\frac{\nabla^2}{2} + u_{c,f}(\vec{r}) \right] \phi_\alpha^{KS}(\vec{r}) = e_\alpha^{KS} \phi_\alpha^{KS}(\vec{r}),
$$

(69)

met uiteraard een gelijkwaardige vergelijking voor de hermitisch toegevoegde orbitaal $\phi_\alpha^{KS}$. In deze vergelijkingen hebben we de effectieve potentiaal ingevoerd,

$$
u_{c,f}(\vec{r}) = v(\vec{r}) + v_J(\vec{r}) + v_{xc}(\vec{r}),
$$

(70)

die de externe potentiaal $v(\vec{r})$ bevat die op het interagerend systeem inwerkt, een potentiaal afgeleid van de directe Coulomb interactie (de Hartree term)

$$
v_J(\vec{r}) = \int d^3 r' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|},
$$

(71)

en de uitwisselingscorrelatiepotentiaal

$$
v_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})},
$$

(72)

die in dit werk een centrale rol inneemt.

Nu hebben we de exacte gedaante gevonden voor de externe potentiaal die we op een fictief niet-interagerend systeem beschreven door vergelijkingen (69) moeten laten inwerken om de correcte interagerende dichtheid van het oorspronkelijk systeem te vinden. Er is echter een aantal problemen met deze effectieve potentiaal.

Eerst en vooral kennen we de dichtheid van het interagerend systeem niet, hoewel die vereist is in de Hartree potentiaal in vergelijking (70). Ook is het duidelijk uit de definitie (5.52) dat in het algemeen $v_{xc}(\vec{r})$ eveneens dichthedafhankelijk zal zijn. Dit houdt in dat de KS vergelijkingen zelf-consistent moeten worden opgelost (zie schema hieronder). Er is nog een tweede probleme dat uiterst belangrijk is voor het voorspellend vermogen van DFT: we weten niet wat de expliciete gedaante is van de uitwisselingscorrelatiefunctieaal $E_{xc}[\rho]$ in termen van de dichtheid en bijgevolg is ook $v_{xc}(\vec{r})$ niet gekend. Daarom maakt men in praktische berekeningen gebruik
van benaderende vormen voor deze potentiaal (er zijn verschillende benaderingen ontwikkeld voor een waaier van toepassingen). Meer uitleg over deze benaderende functionalen wordt gegeven in hoofdstuk 5.

Samenvattend stellen we het zelf-consistente schema voor om de KS vergelijkingen op te lossen. Vooraf moeten we natuurlijk een bepaalde benaderende vorm kiezen voor de uitwisselingscorrelatiepotentiaal (deze vorm blijft dan vast over de iteraties). Om de dichtheidsafhankelijkheid van deze potentiaal te benadrukken, nemen we tijdelijk de notatie \( v_\text{xc}(\rho) \) aan. Het KS schema ziet er dan als volgt uit:

(i) Start met een initiële schatting voor de golfuncties \( \phi^K_S(\vec{r}) \) (b.v. waterstofachtige of Hartree-Fock golfuncties).

(ii) Construeer de dichtheid \( \rho(\vec{r}) = \sum_{\alpha=1}^{N} |\phi^K_S(\vec{r})|^2 \).

(iii) Construeer de effectieve potentiaal (met de vaste benaderende vorm voor de uitwisselingscorrelatiepotentiaal) \( v_{\text{eff}}(\vec{r}) = v(\vec{r}) + v_f(\vec{r}) + v_{\text{xc}}(\rho, \vec{r}) \).

(iv) Maak een update van de set ééndelige orbitalen \( \{\phi^K_S(\vec{r})\} \) door de KS vergelijkingen \( -\frac{\nabla^2}{2} + v_{\text{eff}}(\vec{r}) \) \( \phi^K_S(\vec{r}) = \epsilon^K_S \phi^K_S(\vec{r}) \) op te lossen.

(v) Herhaal het schema vanaf stap (ii) tot convergentie in de ééndeligeorbitalen en ééndelijkgotriënergieën optreedt.

De zelf-consistente aanpak via de golfuncties van het KS schema rekent af met enkele gebreken van de Hohenberg-Kohn theorie. Zo komt de schilstructuren in de radiale dichtheid te voorschijn en worden stabiele configuraties voor moleculen voorop. Uiteraard is het kiezen van de gepaste uitwisselingscorrelatiepotentiaal soms een moeilijke opdracht, maar die is wel van cruciaal belang voor de accuraatheid van de voorspellingen. In de wetenschappelijke gemeenschap wordt dan ook uitgezocht welke benaderingen goed zijn voor welke problemen (zie b.v. "The Computational Chemistry Comparison and Benchmark Database" [157]).

Tot slot bespreken we nog even de schijnbare paradox die verscholen zit in de centrale voorwaarde in het KS schema, nl. dat dichtheid van interagerend en niet-interagerend systeem hetzelfde moeten zijn. Hoe kunnen we nu te weten komen of dit na convergentie werkelijk zo is als we de dichtheid van het interagerend systeem proberen te zoeken a.h.v. het KS schema? Het antwoord op deze vraag ligt vervat in de uitwisselingscorrelatiepotentiaal en de zelf-consistente procedure van het KS schema. De exacte uitwisselingscorrelatiepotentiaal giet alle tweedelige interacties in de vorm van een ééndelijkgotriëntial en stelt ons in staat om een interagerend veldeldijkssysteem te bestuderen a.h.v. ééndeligevergelijkingen. Door de zelf-consistente aanpak, kunnen we intuïtief inzien dat over de iteraties, de kwantum-mechanische veldeldijjseffecten die in de effectieve potentiaal aanwezig zijn gradueel
in de dichtheid van het KS systeem worden ingezet. Bij convergente hebben we dan de (unieke) effectieve potentiaal gevonden die ervoor zorgt dat de dichtheid van het niet-interagerend systeem die van het interagerend systeem simuliert (de unieiteit van de potentiaal volgt uit het eerste Hohenberg-Kohn theorema toegepast op het niet-interagerend systeem). In de praktijk hangt het af van de kwaliteit van de benaderende uitwisselingscorrelatiepotentiaal hoe goed deze simulatie zal lijken op de experimentele dichtheid.

Tenslotte vermelden we nog dat we de totale energie van het interagerend systeem kunnen vinden via de betrekking

\[ E[\rho] = \sum_{\alpha=1}^{N} \epsilon_{\alpha} - \frac{1}{2} \int d^{3}r_{1} \int d^{3}r_{2} \frac{\rho(\vec{r}_{1})\rho(\vec{r}_{2})}{|\vec{r}_{1} - \vec{r}_{2}|} - \int d^{3}r \ v_{xc}(\vec{r}) \ \rho(\vec{r}) + E_{xc}[\rho]. \] (73)

6 Microscopische basis voor DFT via Greense functie technieken.

In deze paragraaf maken we de connectie tussen het Greense functie formalisme en DFT. Uit de Greense functie berekening kunnen we de dichtheid halen die alle tweede orde correlaties van het Dyson(2) schema in zich draagt [zie vergelijking (11)]. We hebben dan een algorithm nodig dat de uitwisselingscorrelatiepotentiële geeft die in DFT nodig zou zijn om dezelfde dichtheid te reproduceren. Voor dit zogenaamde inversie-proces zijn tal van algoritmes voorgesteld (zie b.v. [279]-[287]), maar deze zijn soms maar beperkt toepasbaar op een paar kleine systemen zoals helium, beryllië of neon. Van de meer algemene schema’s vermelden we het dichtheidsrespons-algoritme (zie [266] en [269]) en de methode van Zhao, Morrison en Parr (ZMP; zie Ref. [286]). Eerstgenoemde methode genereert de KS potentiaal door een integraalvergelijking op te lossen voor de inverse responsfunctie van het KS systeem, die variaties in de dichtheid relateert aan variaties in de potentiaal. Laatstgenoemd schema minimaliseert de niet-interagerende kinetische energie onder de restrictie dat de KS dichtheid gelijk moet zijn aan de inputdichtheid (b.v. de Greense functie dichtheid). Deze twee methodes hebben een sterke fysische onderbouw, maar zijn tamelijk ingewikkeld om op een numeriek stabiele manier te implementeren.

Daarom zullen we in deze paragraaf een eenvoudig en robuust algorithm voorstellen om het inversieprobleem in de coördinatenruimte op te lossen. Het schema zal worden toegepast op de Greense functie dichtheden, maar is bruikbaar voor eender welke atomaire dichtheid. Bovendien zijn de basisprincipes algemeen geldig en verwachten we dat het schema ook zal werken voor systemen zonder sferische symmetrie.

In onderdeel 6.1 leggen we het algoritme zelf uit, terwijl we in onderdeel 6.2 enkele resultaten bekomen uit de Dyson(2) dichtheid bespreken.
6.1 Het inversie algoritme.

We geven het algoritme in spinonafhankelijke vorm: de spinversie kan worden bekomen door waar gepast de spinindex σ toe te voegen. Zoals steeds in dit werk, worden ook hier atomaire eenheden gebruikt.

In de inleiding tot deze sectie werd al vermeld dat het inversieprobleem erin bestaat voor een gegeven input dichtheid \( \rho^{\text{ref}}(\vec{r}) \) die één ensemble met \( N \) elektronen beschrijft, de unieke potentiaal \( v_\sigma(\vec{r}) \) te vinden die deze dichtheid oplevert d.m.v. de oplossing van de KS vergelijkingen.

Hier wordt het inversieprobleem opgelost in de coördinatenruimte m.b.v. een iteratief schema. In de effectieve potentiaal (70) wordt alleen de uitwisselingscorrelatiepotentiaal steeds opnieuw geëvalueerd over de iteraties, de Hartree term blijft vast en wordt aan het begin van het algoritme bepaald met de input dichtheid \( \rho^{\text{ref}}(\vec{r}) \). Vermits we hier atomaire systemen bestuderen, is enkel de radiale vrijheidsgraad \( r \) van belang en zullen we het hoekafhankelijk deel in \( \vec{r} \) niet meer vermelden.

We initialiseren de uitwisselingscorrelatiepotentiaal met de Dirac potentiaal [182]:

\[
v_\sigma^{(0)}(r) = - \left[ \frac{3}{\pi} \rho^{\text{ref}}(r) \right]^{\frac{1}{2}}.
\]

De Dirac potentiaal geeft een redelijke benadering voor het uitwisselingsgedeelte, wat de dominante contributie is tot de uitwisselingscorrelatiepotentiaal.

Onderstel dat we de uitwisselingscorrelatiepotentiaal van iteratie \( n \) hebben, dan lossen we de KS vergelijkingen (69) corresponderend met deze potentiaal op in de coördinatenruimte en bepalen we de KS elektronendichtheid:

\[
\rho^{KS[n]}(r) = \sum_{i=1}^{N} | \phi_i^{KS[n]}(r) |^2.
\]

De uitwisselingscorrelatiepotentiaal van de volgende iteratie wordt dan bekomen door volgende correctie toe te passen:

\[
v_\sigma^{(n+1)}(r) = v_\sigma^{(n)}(r) + \alpha r \left[ \rho^{KS[n]}(r) - \rho^{\text{ref}}(r) \right] + \left[ I_{KS}^{(n)} - I_{\text{ref}} \right] f(r).
\]

De derde term in deze vergelijking bevat de ionisatie energie \( I_{KS}^{(n)} = -\epsilon_{\text{ion}}^{KS(n)} \), waar \( \epsilon_{\text{ion}}^{KS(n)} \) de energie is van de hoogst bezette KS orbitala in iteratie \( n \). De ionisatie energie \( I_{\text{ref}} \) wordt eenduidig bepaald door het asymptotische gedrag van de inputdichtheid [zie vergelijking (78)]. Verderop gaan we dieper in op vergelijking (76).

Met de update (76) voor de uitwisselingscorrelatiepotentiaal kunnen de KS vergelijking opnieuw worden opgelost. Dit schema wordt herhaald tot convergentie is bereikt. Als convergentiecriterium nemen we

\[
4\pi \int dr \ r^2 \ | \rho^{KS[n]}(r) - \rho^{\text{ref}}(r) | < \Delta,
\]

(77)
met $\Delta = 10^{-5}$. Voor de open-schil inversie wordt de convergentievoorwaarde opgelegd aan beide spindichtheiden afzonderlijk en stellen we $\Delta_r = 5 \times 10^{-6}$.

Eender welke redelijke dichtheid $\rho_{ref}(r)$ kan worden gebruikt als input voor het algoritme. Om echter een goed asymptotisch gedrag voor de KS dichtheid en de uitwisselingscorrelatiepotentiaal te hebben, moet de inputdichtheid natuurlijk ook het correcte asymptotische gedrag hebben. Voor een atoom met een niet-ontaarde grondtoestand kan worden aangetoond dat het asymptotische gedrag van de dichtheid gegeven wordt door [133]

$$\rho_{ref}(r) \sim e^{-2\kappa r^2(1^{1/3})},$$

waarin $\kappa = \sqrt{2T_{ref}}$. Merk op dat de ionisatie energie, zoals hierboven vermeld, in principe bepaald wordt door het asymptotische gedrag van de inputdichtheid $\rho_{ref}$.

Laat ons nu even terugkeren naar het update schema van vergelijking (76). De fysische interpretatie van de eerste correctieterm is de volgende: als de KS dichtheid van iteratie $n$ groter is dan de referentiedichtheid in een bepaald gebied in de ruimte, dan moet de uitwisselingscorrelatiepotentiaal van de volgende iteratie repulsiever worden in dat gebied. Op die manier wordt de KS dichtheid gedwongen om de referentievorm aan te nemen.

In uitdrukking (76) is de waarde van de (positieve) parameters $\alpha$ en $\beta$ over het algemeen niet cruciaal voor de finale geconvergerde vorm van de potentiaal, maar kan deze een belangrijke invloed hebben op het aantal iteraties dat nodig is om convergentie te bekomen. De parameter $\alpha$ bepaalt het totale gewicht van de lokale correctie op de uitwisselingscorrelatiepotentiaal. De parameter $\beta$ verhoogt het gewicht wanneer $r$ groot wordt, in welk gebied de correctie anders heel klein wordt. Convergentie werd bekomen voor $\alpha$ tussen 0.5 en 3.5 atomaire eenheden, terwijl de waarde voor $\beta$ in geval van de gesloten schil atomen kon variëren tussen nul en drie. In het open schil geval, was de keuze van $\beta$ delicater, maar we vonden goede resultaten voor $\beta \approx 2$ in geval van B en C, terwijl voor N, O en F $\beta \approx 1.5$ beter leek.

De tweede term in vergelijking (76) is strikt genomen niet nodig om convergentie te bereiken naar een uitwisselingscorrelatiepotentiaal met een correct asymptotisch gedrag (zie onderdeel 6.2). Zonder de tweede term kan de absolute waarde van de hoogst bezette KS eigenwaarde echter wat afwijken van de waarde voor $T_{ref}$ die correspondeert met de staart van de inputdichtheid. Dit komt omdat in het asymptotische gebied de eerste correctieterm (zelfs met de extra factor $r^3$) klein is en dus een groot aantal iteraties nodig zou zijn om een overeenstemming tussen de ionisatie energieën te bekomen. Om aan dit probleem te verhelpen werd de tweede term ingevoerd. De factor $f(r)$ in de tweede term heeft de volgende vorm

$$f(r) = \theta(1-r) \, r^\gamma + \frac{\theta(r-1)}{r^\delta}.$$  

(79)
De stapfuncties \([\theta(x)]\) maken een continue overgang mogelijk tussen de twee termen in \(f(r)\) op een afstand van één Bohrsestraal. Wanneer beïnvloeden de parameters \(\gamma\) en \(\delta\) alleen de snelheid waarmee convergentie wordt bereikt en niet het uiteindelijk resultaat (hun waarde moet uiteraard wel positief zijn). In de berekeningen gebruikten we de waarde \(\gamma \approx 5\) voor de gesloten schil atomen en \(\gamma \approx 1\) voor de open schil atomen. De parameter \(\delta\) kan op \(\delta \approx 3\) worden genomen in beide gevallen. Beide parameters kunnen echter gevarieerd worden binnen een groot bereik, zonder de finale vorm van de geconvergeerde potentiaal te beïnvloeden.

![Graph](image)

Figuur 6: Uitwisselingspotentiaal gegenereerd met de HF dichtheid uit Fig. 7.

### 6.2 Resultaten van het inversie algoritme.

Het inversie algoritme werd eerst getest op Hartree-Fock (HF) niveau, waarbij HF dichtheden gegenereerd in de coördinatenruimte (zie paragraaf 3) worden gebruikt als input. De HF dichtheid levert met bovenstaand algoritme een potentiaal op die sterk lijkt op die van de Optimized-Effective-Potential (OEP) methode waarbij enkel exacte uitwisseling ("exchange") in rekening wordt gebracht (geen correlaties). Een voorbeeld is gegeven in Fig. 6, die kan worden vergeleken met de OEP uitwisselingspotentiaal van Ref. [289].

Het inversieschema kan nu worden toegepast op uitwisseling en correlatie effecten door de Dyson(2) dichtheden te gebruiken als input in het schema. Hier treedt echter een probleem op dat wordt veroorzaakt door het invoegen van de muur in het Dyson(1) schema. Hoewel deze muur de energetische aspecten in het schema niet beïnvloedt, is er wel een invloed van de muur op de dichtheid. Het inversie schema is uiterst gevoelig (dit is een algemene vaststelling en is niet gebonden aan
Samenvatting. *Ab initio studie van Dichtheidsfunctionaaltheorie via Greense functies.*

Figuur 7: Hartree-Fock (streepjeslijn), Dyson(2) (punt-streeplijn) en gecorrigeerde Dyson(2) (volle lijn) dichtheid voor neon.

de huidige implementatie, zie b.v. [273]) en bijgevolg is een volledig correct asymptotisch gedrag vereist om een aanvaardbare potentiaal te verkrijgen. Daarom wordt in de omgeving van het punt waar de muur staat aan de dichtheid het correcte asymptotische gedrag opgelegd [vergelijking (78), waarbij $I_{\text{ref}}$ de eerste ionisatie energie voorstelt zoals voorspeld door het Dyson(2) schema]. Aangezien kleine trillingen in de dichtheid sterk vergroot worden in de uitwisselingscorrelatiepotentiaal werd er bij deze correctie voor gezorgd dat de eerste, tweede en derde afgeleide van dichtheid continu zijn in de extrapolatie. Aangezien de dichtheid al in het asymptotische regime is op de positie van de muur, beïnvloeden we met deze correctie enkel het asymptotische gebied van de dichtheid: correlatiebijdragen tot de dichtheid worden dus niet aangetast. Een voorbeeld van de correctie wordt gegeven in Fig. 7. De asymptotische regimes van HF en Dyson(2) dichtheden in deze figuur wijken af doordat de ionisatie energie in beide systemen verschilt.

Het inversie algoritme is toegepast op de gesloten schil atomen (He, Be, Ne, Mg en Ar) en de open schil systemen (B, C, N, O en F) van de Greense functie berekeningen. We bespreken hier enkele van de resultaten (een volledig overzicht kan worden gevonden in hoofdstuk 6).

We merken eerst op dat we bij convergentie niet alleen de input dichtheid op accurate wijze reproduceren, maar dat ook de hoogste bezette KS eigenwaarde samenvalt met de Dyson(2) ionisatie energie (tot op een nauwkeurigheid van $10^{-7}$ atomaire eenheden of beter). Zoals we zullen zien, vertonen de potentiaal het correcte asymptotische gedrag $\sim \frac{1}{r}$. Dit gedrag is niet opgelegd maar wordt automatisch door het schema gegenereerd op voorwaarde dat de dichtheid het correcte asymptotische

Figuur 8: Uitwisselingscorrelatiepotential $v_{xc}(r)$ (bovenste figuur) en $r \times v_{xc}(r)$ (onderste figuur) voor He en Be gegenereerd door het inversie algoritme van dit werk en ter vergelijking ook de resultaten van Refs. [276], [290]: volle lijn: He (dit werk), streepjeslijn: He (“high-level” berekening [276]); puntlijn: Be (dit werk), puntstreeplijn: Be (KMC [290]).

gedrag heeft [vergelijking (78)].

In Fig. 8 en 9 tonen we enkele uitwisselingscorrelatiepotentialen afkomstig van het schema toegepast op de Greense functie berekeningen. De bovenste figuur bevat telkens de potentiaal op zich, terwijl de onderste figuur $r \times v_{xc}(r)$ weergeeft om beter het correcte asymptotische gedrag van de dichtheid aan te duiden. Ter vergelijking includeren we ook de uitwisselingscorrelatiepotentialen gegenereerd door “high-level” berekeningen: voor helium geven we de “high-level” potentiaal bekomen door Umrigar en Gonze in Ref. [276] en voor beryllium en neon is een kwantum-Monte-Carlo (KMC) potentiaal ter beschikking gesteld door dezelfde auteurs [275] en door Filippi, Umrigar en Gonze [273]. Het is duidelijk dat onze Dyson(2) potentialen goed aansluiten bij deze “referentiepotentialen”, vooral in geval van helium.

In Fig. 10 en 11 geven we de spinpotentialen voor respectievelijk koolstof en zuurstof. Zoals bij de gesloten schil atomen zijn zowel $v_{xc}(r)$ als $r \times v_{xc}(r)$ aangegeven.
Figuur 9: Potentialen voor Ne [$v_{xc}(r)$ (bovenste figuur) en $r \times v_{xc}(r)$ (onderste figuur)]; volle lijn is dit werk, streepjeslijn is de KMC potentiaal [290].

Samenvattend kunnen we stellen dat alle potentiaal-noties systematisch het correcte asymptotische gedrag vertonen. Ook zien we dat de uitwisselingscorrelatiepotentiaal in de oorsprong een eindige waarde geeft, overeenkomstig het theoretisch gedrag van de correcte potentiaal (zie hoofdstuk 5) en de suggestie van Morrison et al. [292].

Een ander karakteristiek verschijnsel dat in alle potentiaal-noties opduikt, zijn de pieken op tussenschil posities. Deze pieken kunnen theoretisch worden verklaard: zie Refs. [293]-[295].

Aangezien de uitwisselingscorrelatiepotentiaal die met het voorgestelde algoritme worden bekeken de inputdicthet lijn bijna perfect reproduceren, kunnen we aannemen dat alle correlaties die in de Dyson(2) dichtheid besloten liggen, ook geïncorporeerd zijn in de potentiaal. De gegenereerde potentiaal kunnen worden gebruikt in een aantal toepassingen, zoals het geven van een microscopische basis aan hedendaagse functionalen die in DFT worden aangewend. Twee mogelijke toepassingen, nl. een studie van de uitwisselingscorrelatie-energie en een herfis van een bestaande functional, worden besproken in hoofdstuk 6. Hier geven we enkel de bespreking van de uitwisselingscorrelatie-energie en de samenstellende delen ervan.
Figuur 10: Uitwisselingscorrelatiepotentiaal $v_{xc}(r)$ (bovenste figuur) en $r \times v_{xc}(r)$ (onderste figuur) afkomstig van dit werk voor C: meerderheidsspin is in volle lijn, minderheidsspin in streepjeslijn.

De uitwisselingscorrelatie-energie is gedefinieerd als

$$E_{xc}[\rho] = (T[\rho] - T_{x}[\rho]) + (W[\rho] - J[\rho]) = T_{x}[\rho] + (W[\rho] - J[\rho]),$$

waarbij $E_{xc}[\rho]$ kan bekomen worden via

$$E_{xc}[\rho] = E_{0(A)} - \sum_{i^{occ}} \epsilon_{i}^{KS} + J[\rho] + 4\pi \sum_{\sigma} \int dr \ r^{2} \ v_{impul}^{\sigma}(r) \ \rho_{\sigma}(r),$$

met $E_{0(A)}$ de Dyson(2) grondtoestandsenergie van het velelektronensysteem $A$, terwijl de KS eigenwaarden $\epsilon_{i}^{KS}$ gegenereerd worden door het inversieschema $[v_{impul}^{\sigma}(r)]$ is de uitwisselingscorrelatiepotentiaal verkregen met het inversie-algoritme uit de Dyson(2) dichtheid.

Het uitwisselingsstuk $E_{x}[\rho]$ is berekend via (waarbij $|\Phi_{0}\rangle$ staat voor de Slater-
Figuur 11: Uitwisselingscorrelatiepotentialen $\nu_{2e}(r)$ (bovenste figuur) en $r \times \nu_{2e}(r)$ (onderste figuur) afkomstig van dit werk voor O: meerheidsspin is in volle lijn, minderheidsspin in streepjeslijn.

determinant opgebouwd met de $N$ laagste KS orbitalen:

$$E_x [\rho] = \langle \Phi_0 | \hat{W} | \Phi_0 \rangle - \frac{1}{2} \int d^3 r_1 \int d^3 r_2 \frac{\rho(\vec{r}_1) \rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

$$= -\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{m_{i,j}} \int d^3 r_1 \int d^3 r_2 \phi_i^{KS}(\vec{r}_1) \phi_j^{KS}(\vec{r}_2) \phi_i^{KS}(\vec{r}_1) \phi_j^{KS}(\vec{r}_2) \frac{\delta_{m_{i,j}}}{|\vec{r}_1 - \vec{r}_2|}.$$

(82)

Uit Tabel 6 is het duidelijk dat het uitwisselingsdeel het grootste deel van de kwantummechanische interacties in zich draagt. Toch zijn de correlatie-invloeden ook belangrijk om een accurate beschrijving van het interagerend veeleitjessysteem te geven met behulp van DFT. Bij de evaluatie van $T_s[\rho]$ werd het viriaal theorema gebruikt: $T_c[\rho] = T[\rho] - T_s[\rho] = -E[\rho] - T_s[\rho]$, waar $E[\rho]$ de exacte grondtoestandsenergie van het interagerende veeleitjessysteem voorstelt [die werd benaderd door de Dyson(2) grondtoestandsenergie]. Uit de tabel leiden we ook af dat $T_c$ kleiner is.

Tabel 6: Schattingen van \( E_{xc}[\rho] \), vergelijking (81), samen met de pure uitwisselingsenergie \( E_x[\rho] \), vergelijking (82), de totale correlatie energie \( E_c[\rho] = E_{xc}[\rho] - E_x[\rho] \) en de kinetische contributie \( T_c[\rho] \) tot de correlaties-energie. De waarden van Whittingham en Burke (WB) voor \( T_c[\rho] \) werden bekomen via Ref. [296], en die van Morrison en Zhao (MZ) zijn terug te vinden in [292].

<table>
<thead>
<tr>
<th>( E_{xc}[\rho] )</th>
<th>( E_x[\rho] )</th>
<th>( E_c[\rho] )</th>
<th>( T_c[\rho] ) (WB)</th>
<th>( T_c[\rho] ) (MZ)</th>
<th>( T_c[\rho] ) [Dyson(2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>-1.0602</td>
<td>-1.0229</td>
<td>-0.0373</td>
<td>0.037</td>
<td>0.0478</td>
</tr>
<tr>
<td>Li</td>
<td>-2.7299</td>
<td>-2.6677</td>
<td>-0.0622</td>
<td>0.031</td>
<td>0.074</td>
</tr>
<tr>
<td>Be</td>
<td>-3.8134</td>
<td>-3.7483</td>
<td>-0.0651</td>
<td>0.058</td>
<td>0.095</td>
</tr>
<tr>
<td>B</td>
<td>-5.1411</td>
<td>-5.0495</td>
<td>-0.0916</td>
<td>0.130</td>
<td>0.12</td>
</tr>
<tr>
<td>C</td>
<td>-6.7336</td>
<td>-6.5923</td>
<td>-0.1413</td>
<td>0.149</td>
<td>0.15</td>
</tr>
<tr>
<td>N</td>
<td>-8.3584</td>
<td>-8.1720</td>
<td>-0.1864</td>
<td>0.239</td>
<td>0.19</td>
</tr>
<tr>
<td>O</td>
<td>-10.2460</td>
<td>-9.9920</td>
<td>-0.2540</td>
<td>0.327</td>
<td>0.24</td>
</tr>
<tr>
<td>F</td>
<td>-12.4114</td>
<td>-12.0720</td>
<td>-0.3394</td>
<td>0.401</td>
<td>0.30</td>
</tr>
<tr>
<td>Ne</td>
<td>0.372</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>-16.2964</td>
<td>-15.9611</td>
<td>-0.3353</td>
<td>0.364</td>
<td>0.34</td>
</tr>
<tr>
<td>Al</td>
<td>0.369</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>0.392</td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>0.429</td>
<td>0.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.476</td>
<td>0.39</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.532</td>
<td>0.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>-30.7461</td>
<td>-30.1437</td>
<td>-0.6024</td>
<td>0.589</td>
<td>0.21</td>
</tr>
</tbody>
</table>

dan de correlatiebijdrage \( E_{cc}^{\rho} = W[\rho] - J[\rho] - E_x[\rho] \) en dat ruwweg geldt:

\[
T_c[\rho] \approx -\frac{1}{2} E_{cc}^{\rho}[\rho] \approx -E_c[\rho],
\]

waar \( E_c[\rho] = E_{xc}[\rho] - E_x[\rho] \) de totale correlatie energie binnen het Kohn-Sham schema is. Verder merken we op dat \( T_c \) berekend wordt door het verschil te nemen van twee grote getallen. Daardoor ligt de nauwkeurigheid niet zo hoog en kunnen de verschillende voorspellingen voor deze grootheid soms veel afwijken.

Voor de bespreking van het herfitten van de functionaal alsook de veralgemening van de Kohn-Sham vergelijkingen op basis van Greense functie theorie verwijzen we de geïnteresseerde lezer naar hoofdstuk 6.
Appendix A

The atomic-units measurement system.

In the following table, we give an overview of the conversion from atomic units to SI units for some observables [306].

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Interpretation</th>
<th>Atomic units</th>
<th>SI-units</th>
</tr>
</thead>
<tbody>
<tr>
<td>elementary charge</td>
<td>$e = 1$</td>
<td>$1.6021766241 \times 10^{-19}$ C</td>
<td></td>
</tr>
<tr>
<td>electron rest mass</td>
<td>$m_e = 1$</td>
<td>$9.109381884 \times 10^{-31}$ kg</td>
<td></td>
</tr>
<tr>
<td>angular momentum</td>
<td>reduced Planck's constant</td>
<td>$\hbar = 1$</td>
<td>$1.05457158 \times 10^{-34}$ J s</td>
</tr>
<tr>
<td>vacuum permittivity</td>
<td>$\varepsilon_0 = 4\pi\varepsilon_0 = 1$</td>
<td>$1.11265011 \times 10^{10}$ $C^2 J^{-1} m^{-1}$</td>
<td></td>
</tr>
<tr>
<td>distance</td>
<td>Bohr's radius</td>
<td>$a_0 = \frac{\hbar}{m_e c}$</td>
<td>$0.5291772083 \times 10^{-10}$ m</td>
</tr>
<tr>
<td>energy</td>
<td>twice the 1s energy of H (hartree)</td>
<td>$m_e^* a_0^* = \frac{m_e}{\varepsilon_0} a_0 = 1$</td>
<td>$4.35974381 \times 10^{-18}$ J</td>
</tr>
<tr>
<td></td>
<td>period of the 1s-electron in H</td>
<td>$\frac{m_e}{e} a_e = 1$</td>
<td>$2.418843265001 \times 10^{-17}$ s</td>
</tr>
<tr>
<td>velocity</td>
<td>velocity of the 1s-electron in H</td>
<td>$\frac{e}{m_e c} = 1$</td>
<td>$2.1876912529 \times 10^6$ m s$^{-1}$</td>
</tr>
<tr>
<td>electrical potential</td>
<td>potential energy of the 1s-electron in H</td>
<td>$\frac{Ze^2}{\hbar^2} = \frac{e}{\varepsilon_0} = 1$</td>
<td>$27.2113834$ V</td>
</tr>
<tr>
<td>magnetic dipole moment</td>
<td>twice the Bohr magneton</td>
<td>$\frac{Ze}{m_e} = 1$</td>
<td>$1.8548017991 \times 10^{-23}$ J T$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$= 11.5767635 \times 10^{-5}$ eV T$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>

Atomic units are mainly used because in this system most common constants

247
(e.g. the charge and mass of the electron, the reduced Planck's constant, Bohr's radius, ...) are put equal to unity and, consequently, theoretical expressions are much simplified.
Appendix B

Feynman rules in configuration-energy space.

In the diagrams we consider here, time is implicitly present and goes forward in the upward direction of the diagram. However, the propagator lines can denote both a particle or a hole Green’s function. The following Feynman rules (in atomic units) apply for the term of order $n$ in the expansion of the Green’s function

$$ G_{\alpha\beta}(E) = \sum_{n=0}^{\infty} G^{(n)}_{\alpha\beta}(E) = G^{(0)}_{\alpha\beta}(E) \delta_{\alpha\beta} + \sum_{\alpha' \beta'} \delta_{\alpha\alpha'} G^{(0)}_{\alpha\alpha'}(E) \Sigma_{\alpha' \beta'}(E) G_{\beta' \beta}(E). \quad (B.1) $$

![Figure B.1: The zero-order propagator $G^{(0)}_{\alpha\beta}(E)$.](image)

- A Green’s function diagram of order $n$ consists of all possible combinations of $n$ (antisymmetrized) interaction lines and $(2n + 1)$ zero-order Green’s function $G^{(0)}_{\alpha\beta}(E)$ (in Fig. B.1, this zero-order propagator is represented).
If we remove the two external fermion lines of the Green’s function diagram, we obtain the \(n^{th}\) order contribution to the self-energy. Note that at each interaction end point (\textit{vertex}), an incoming and outgoing fermion line must be present, such that the \((2n - 1)\) internal propagators are used to interconnect the \(n\) interaction lines.

The combinations of zero-order propagators and interaction lines to be taken into account in the \(n^{th}\) order Green’s function are restricted, however. First, only connected diagrams are to be considered, i.e. diagrams that only consist of pieces that are linked to the external fermion lines. Second, the interactions are assumed to be antisymmetrized, which indicates that the configuration of a direct diagram also includes the exchange contribution. A diagram that can be derived by an exchange operation on an interaction line, is therefore to be discarded from a graph that is already considered in the combinations. An exchange operation consists of interchanging either the two incoming or the two outgoing fermion lines on an interaction line (Fig. B.2).

![Figure B.2: Equivalent diagrams by means of an exchange operation on an interaction line.](image)

Third, of the class of equivalent diagrams generated by a permutation of the time indices at which the interactions take place, only one representative is required.

- We assign one single-particle label \(\gamma_j\) and \(\gamma_i\) to the beginning and end point of the fermion line respectively. In the analytical expression corresponding to the Feynman diagram, this labeled fermion line gives rise to a factor \(G^{(0)}_{\gamma_i\gamma_j}(E_k)\). An internal line carries an energy \(E_k\), the two external lines of the propagator \(G^{(n)}_{\alpha\beta}(E)\) of course have a fixed energy \(E\).

- Add a direction and an energy \(E_l\) to all interaction lines. Due to the symmetry of the two-body interaction \(W\) for the interchange of the two interacting fermions, this artificial direction does not restrict the generality of the discussion. We can interpret the direction of the arrow as the direction of the foton that is exchanged with energy \(E_l\) between the two fermions. Energy conservation in each vertex imposes restrictions on the energy carried by the interaction.
and the fermion lines meeting in the vertex. This leads to \( n \) internal degrees of freedom. The interaction line is labeled using the indices of the incoming and outgoing Green's functions and contributes a factor \( \langle \gamma_i \gamma_j \mid W \mid \gamma_k \gamma_l \rangle_{as} \) in the translation of Feynman diagram to the analytic expression (see also Fig. B.3).

\[
\begin{array}{ccc}
\begin{array}{c}
\text{interaction line}
\end{array}
& = & \begin{array}{c}
W \end{array}
\end{array}
\]

Figure B.3: Analytical expression for the interaction line.

- Multiply by a factor \( e^{\eta E_k} \) for each loop, i.e. a sequence of propagator lines beginning and ending at the same vertex. Here, \( \eta \) is an infinitesimal positive convergence parameter and \( E_k \) is the internal energy of the loop.

- Perform a summation over all internal labels \( \gamma_i \) and integrate over the \( n \) internal energy degrees of freedom \( E_k \). Note that no integration over the fixed energy \( E \) of the two external fermion lines is implied here.

- Include a factor \( \frac{1}{2} \) for each pair of equivalent fermion lines. These are propagators that start and end at the same interaction lines (see Fig. B.4).

\[
\begin{array}{ccc}
\begin{array}{c}
\text{fermion lines}
\end{array}
& \leftrightarrow & \begin{array}{c}
\text{fermion lines}
\end{array}
\end{array}
\]

Figure B.4: The fermion lines \( G^{(0)}_{\alpha \gamma} \) and \( G^{(0)}_{\beta \delta} \) are equivalent (left figure: particle case; right figure: hole case).

- Include a factor \( (-1)^F \left( \frac{4}{\pi} \right)^n \), where \( F \) is the number of loops present in the \( n^{th} \) order diagram.
Appendix C

Positive definiteness of the Fock operator.

In this appendix, we focus on a special property of the Fock operator, namely its positive definiteness. We recall that the action of the nonlocal Fock potential on the wave function $\varphi_\alpha(\vec{r})$ is defined as

$$[\hat{V}_F \varphi_\alpha](\vec{r}) = \sum_{\alpha'(\text{occ.})} \int d^3r' \frac{\varphi_{\alpha'}^*(\vec{r}) \varphi_{\alpha'}(\vec{r}') \varphi_\alpha(\vec{r})}{|\vec{r} - \vec{r}'|},$$

where the spin degree of freedom is discarded because it is not relevant to the discussion.

To demonstrate the positive definiteness of the Fock operator (i.e. $X^T \hat{V}_F X > 0$, $\forall X \neq 0$), we concentrate on one term in the sum over the occupied states [see Eq. (C.1)]

$$\mathcal{F} = \int d^3r_1 \int d^3r_2 \ \varphi^*_{\alpha'}(\vec{r}_1) \varphi_{\alpha'}(\vec{r}_1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \varphi_\alpha(\vec{r}_2) \varphi^*_\alpha(\vec{r}_2).$$

(C.2)

It can be written as the expectation value of a nonlocal operator

$$\mathcal{F} = \int d^3r_1 \int d^3r_2 \ \Psi^*(\vec{r}_1) \ g(\vec{r}_1, \vec{r}_2) \ \Psi(\vec{r}_2).$$

(C.3)

Since $g(\vec{r}_1, \vec{r}_2) = g(\vec{r}_1 - \vec{r}_2) = \frac{1}{|\vec{r}_1 - \vec{r}_2|}$, this operator has a spectral decomposition in terms of plane waves:

$$g(\vec{r}_1 - \vec{r}_2) = \int d^3q \ \hat{G}(\vec{q}) \ e^{i\vec{q}.(\vec{r}_1 - \vec{r}_2)},$$

(C.4)

which enables us to write Eq. (C.3) in the following form

$$\mathcal{F} = \int d^3q \ \hat{G}(\vec{q}) \int d^3r_1 \ \Psi^*(\vec{r}_1) \ e^{i\vec{q}.\vec{r}_1} \int d^3r_2 \ \Psi(\vec{r}_2) \ e^{-i\vec{q}.\vec{r}_2}.$$
Since $G(q)$ is evidently positive (the Fourier transform of $\frac{1}{r}$ is proportional to $\frac{1}{q^2}$), we see that the Fock term is positive definite.
Appendix D

Functional calculus.

A functional $F$ ([307], [308]) generalizes the concept of a function and is a key object in variational calculus (see Ref. [309] for an introduction to modern functional analysis). It is defined as the transformation that projects a function to a number:

$$F: \ f(x) \rightarrow F[f], \quad (D.1)$$

where $F[f]$ is a complex number and $f$ is a complex function. We use square brackets to distinguish a functional from a function (denoted by round brackets). More generally, the functional can also be defined acting on more than one function.

Typically, functionals appear in extremum problems. The calculus of variations is a branch of the calculus of functionals: the quantity that is to be extremized (e.g., the total energy) can in most cases be written as the functional of some function(s) (e.g., the density and its derivatives). We require the functional to be stationary with respect to arbitrary variations in these functions and arrive at an Euler-Lagrange equations, from which the extremals (the functions that describe the solution to the problem) can be found. Generally speaking, any boundary condition that restricts the extremization process can be included by introducing the proper Lagrange multiplier. To solve an extremum problem, we usually expand the functional $F$ in a Taylor series in arbitrary (but small) variations $\delta f$ of the function $f$ and put the first-order term equal to zero, which leads to the Euler-Lagrange equations. This first-order term of the expansion of $F[f + \delta f] - F[f]$ is defined as the differential of the functional:

$$\delta F = \int \frac{\delta F}{\delta f(x)} \delta f(x) \, dx. \quad (D.2)$$

This expression introduces the pointwise derivative $\frac{\delta F}{\delta f(x)}$ of a functional $F[f]$ and it is clear that this quantity will be of key importance in any variational problem. Note that the definition of the differential of a functional is a straightforward gen-
eralization of the total differential of a function \( f(x_1, x_2, \ldots, x_N) \):

\[
df = \sum_{i=1}^{N} \frac{\partial f}{\partial x_i} \Delta x_i
\]  

We also stress that according to Eq. (D.2), the dimension (in terms of units of measurement) of the functional derivative may not simply be the quotient of the dimensions of the functional and the function it depends on. Note that in a more general context, the functional derivative of order \( n \) is defined as \( \frac{\delta^n f}{\delta x^a} \frac{\delta f}{\delta x^1} \frac{\delta f(x_1)}{\delta x^2} \ldots \frac{\delta f(x_n)}{\delta x} \).

One way to determine the functional derivative is of course to apply the definition: expand \( F[f + \delta f] - F[f] \) and retain only the term of first order in \( \delta f \). By identifying the expression with Eq. (D.2), the functional derivative can be isolated. Note that the functional derivative \( \frac{\delta f}{\delta x} \) may depend on \( f \) values at points other than \( x \), i.e. \( \frac{\delta f}{\delta x} \) itself can be, for each value of \( x \), a functional of \( f \). A more handsome way to determine the functional derivative will be mentioned later on. However, this second method is, contrary to the first, not always applicable, at least not in its easiest form.

Most properties of functional derivatives are very similar to those of derivatives of functions. Some of the most important properties are:

- **derivative of a sum (linearity):**
  \[
  \frac{\delta (a F_1 + b F_2)}{\delta f(x)} = a \frac{\delta F_1}{\delta f(x)} + b \frac{\delta F_2}{\delta f(x)},
  \]
  where \( a \) and \( b \) are (complex) constants and \( F_1 \) and \( F_2 \) are functionals of \( f \).

- **derivative of a product:**
  \[
  \frac{\delta (F_1 F_2)}{\delta f(x)} = \frac{\delta F_1}{\delta f(x)} F_2 + F_1 \frac{\delta F_2}{\delta f(x)},
  \]

- **chain rule:** Suppose that \( F \) is a functional in a function \( f \), which in its turn also depends (pointwisely) on a function: \( f(x) = f[g(x), x] \) (for each point \( x \), \( f \) in turn is a functional of \( g \)). Then the following rule applies for the derivative of \( F \) with respect to \( g \):
  \[
  \frac{\delta F}{\delta g(x)} = \int dx' \frac{\delta F}{\delta f(x')} \frac{\delta f(x')}{\delta g(x)},
  \]

- **inversion:** Functionals can only be inverted if a one-to-one mapping exists between functional and function. Suppose that we have a function \( f(x) \) which depends in each point on a function \( g(x) \) and vice versa (note that a function can be regarded as a special case of a functional). As a consequence, we can
derive these two function(s) with respect to each other. The inverse of the functional derivative \( \frac{\delta f(x)}{\delta g(x')} \) is then defined as

\[
\left[ \frac{\delta f(x)}{\delta g(x')} \right]^{-1} = \frac{\delta g(x')}{\delta f(x)}.
\] (D.7)

- **general formula for the functional derivative and special case:** For the general form of the functional \( F[\rho] = \int f(x, \rho(x), \rho^{(1)}(x), \ldots, \rho^{(m)}(x)) \, dx \) [where \( \rho^{(k)}(x) = \frac{d^k \rho(x)}{dx^k} \)], we have the general formula [310]

\[
\frac{\delta F}{\delta \rho(x)} = \frac{\partial f}{\partial \rho} - \frac{d}{dx} \left[ \frac{\partial f}{\partial \rho^{(1)}(x)} \right] + \frac{d^2}{dx^2} \left[ \frac{\partial f}{\partial \rho^{(2)}(x)} \right] - \ldots + (-1)^n \frac{d^n}{dx^n} \left[ \frac{\partial f}{\partial \rho^{(n)}(x)} \right].
\] (D.8)

This equation is valid if the function \( \rho(x) \) vanishes at the boundary of the integration area and can be proven by expanding the function \( f \) in a Taylor series, performing partial integration and identifying with Eq. (D.2). Note that \( \frac{\partial f}{\partial \rho^{(k)}(x)} \) is a partial derivative of the function \( f \) with respect to \( \rho^{(k)}(x) \) but taken when holding \( \rho^{(m)}(x) \) constant for \( m \neq k \). In the three-dimensional case, the operator \( \frac{d}{dx} \) should be replaced by the nabla-operator \( \nabla \).

It is common that the functional \( F \) only depends on \( x \) and the function \( \rho(x) \) [and not the derivatives of \( \rho(x) \)]. For these so-called local functionals the formula (D.8) reduces to

\[
\frac{\delta F}{\delta \rho(x)} = \frac{\partial f}{\partial \rho}.
\] (D.9)

We conclude this discussion on functionals by reviewing the method of finding solutions to an extremum problem. It means that we have to find the extremum of functional \( F \) over all functions \( f(x) \) which are generally assumed to vanish at the boundary of the region where these functions are defined. In this case, the functional should be stationary with respect to small variations of these extremum functions \( f \), or expressed otherwise:

\[
\delta F = \int \frac{\delta F}{\delta f(x)} \delta f(x) \, dx = 0.
\] (D.10)

Provided that the arbitrary testfunctions \( \delta f(x) \) vanish at the borders of the integration interval (fundamental lemma of variational calculus), we can also state this as:

\[
\frac{\delta F}{\delta f(x)} = 0.
\] (D.11)

This equation is called the *Euler-Lagrange equation*: it is a necessary condition for the function \( f \) to be an extremal of the functional \( F \).
Appendix D. Functional calculus

Very often, we must find the extremum of a quantity under certain conditions (e.g., find the wave function that minimizes the total energy, but that has the form of a Slater determinant of single-particle wave functions that are normalized and mutually orthogonal). Suppose that we want to extremize $F[f]$ under the condition that $G[f] = c$, where $c$ is a constant. In this case, we use the method of the Lagrange multipliers and try to reduce the boundary-value problem for $F[f]$ into a free extremum problem for another functional $\Omega[f] = F[f] - \lambda (G[f] - c)$, where $\lambda$ is a constant Lagrange multiplier. The Euler-Lagrange equation then reads

$$
\frac{\delta \Omega}{\delta f(x)} = \frac{\delta F}{\delta f(x)} - \lambda \frac{\delta G}{\delta f(x)} = 0. \tag{D.12}
$$

This equation is then to be solved disregarding the boundary condition, but the resulting extremal will depend on $\lambda$ as a parameter. We can find the correct value for this Lagrange multiplier by substituting the extremal $f$ in the boundary condition $G[f] = c$.

Sometimes, the boundary condition can also vary over the domain where the functional is defined: $G[f, x] = c$ (where $G$ is simultaneously a functional of $f$ and a function of $x$). As can be guessed, we need a Lagrange multiplier that also depends on $x$ to arrive at a free extremum problem. The free problem involves the functional $\Omega[f] = F[f] - \int dx \; \lambda(x) \; (G[f, x] - c)$, from which the following Euler-Lagrange equation is derived

$$
\frac{\delta \Omega}{\delta f(x)} = \frac{\delta F}{\delta f(x)} - \int dx' \; \lambda(x') \frac{\delta G[f, x]}{\delta f(x)} = 0. \tag{D.13}
$$

As indicated above, the Euler-Lagrange equation strictly speaking only represents a necessary condition for functions $f$ that may solve the extremum problem. Once we have found a candidate extremal $f_0$, we still have to verify that the second variation of $F[f]$ is positive (in the case of a minimization problem) at the solution “point” $f_0$

$$
\delta^2 F = \frac{1}{2} \int dx \; \int dx' \left[ \frac{\delta^2 F}{\delta f(x) \delta f(x')} \right]_{f=f_0} \delta f(x) \delta f(x') \geq 0. \tag{D.14}
$$

Equations that represent a sufficient condition for a minimizing function to be an extremal can be found in Ref. [310]. However, when dealing with physical problems, the origin of the problem quite often guarantees that there is only one solution and that the candidate $f_0$ is indeed a minimum.
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Contents

1 Introduction. ................................................................. 7

2 The Green's function formalism. ........................................ 11
  2.1 Introduction. .......................................................... 11
  2.2 One-particle picture. ................................................ 12
  2.3 Green's functions in interacting many-body systems. .......... 15
  2.4 The Dyson equation for the Green's function. .................. 20

3 Self-consistent solution of Dyson's equation: closed-shell atoms. 33
  3.1 Introduction. .......................................................... 33
  3.2 Numerical solution of the HF equations in coordinate-energy space. 35
  3.3 Numerical solution of the second-order Dyson equation. ....... 42
  3.4 The BAGEL approximation. ......................................... 45
     3.4.1 Introduction. .................................................... 45
     3.4.2 Transformation of Dyson's equation into an eigenvalue problem. 49
     3.4.3 Principles of the Lanczos scheme. ........................... 52
     3.4.4 The BAGEL scheme. .......................................... 54
     3.4.5 Extension of the Dyson(2) scheme. .......................... 66
  3.5 Construction of the atomic basis set. ............................. 68
  3.6 Results. .............................................................. 74
     3.6.1 Influence of the second-order correlations on the s,p, strength and total energy. 75
     3.6.2 Single-particle energies and strengths. ...................... 80
     3.6.3 One-particle density and self-energy. ...................... 83

4 Self-consistent solution of Dyson's equation: open-shell atoms. 93
  4.1 Introduction. .......................................................... 93
  4.2 Extended formalism and numerical scheme. ...................... 94
     4.2.1 Mean-field procedure and angular averaging. ............... 94
     4.2.2 Discussion on the averaging scheme. ....................... 98
     4.2.3 Dyson(1) calculation and construction of the basis set. .... 99
     4.2.4 Dyson(2) calculation. ...................................... 100
     4.2.5 Choice of basis set and parameters: case study for carbon. 103
  4.3 Results. .............................................................. 105
  4.4 Summary and conclusions. ......................................... 112
5 Density Functional Theory
5.1 Basic principles of Density Functional Theory ................................ 115
5.2 The electron density .................................................. 117
5.3 The Hohenberg-Kohn theorems ...................................... 121
5.4 The Kohn-Sham scheme ............................................... 129
5.4.1 Introduction ...................................................... 129
5.4.2 Derivation of the Kohn-Sham equations ...................... 130
5.4.3 Ground-state observables in the interacting and the Kohn-
Sham system ......................................................... 134
5.5 Approximations to the exchange-correlation functional ............ 139
5.5.1 Thomas-Fermi and the Local Density approximation ......... 140
5.5.2 The Generalized Gradient Approximation (GGA) ............. 143
5.5.3 The Meta-Generalized Gradient Approximation (meta-GGA) .. 149
5.5.4 Hybrid functionals ............................................... 151
5.5.5 Exchange-correlation functionals with exact asymptotic be-
havior ................................................................. 156
5.6 Exact relations for the exchange-correlation functional .......... 160

6 Ab initio study of DFT based on the Green's function formalism. 165
6.1 Introduction .......................................................... 165
6.2 Inverse-problem algorithm ........................................... 167
6.3 Numerical test of the scheme ....................................... 172
6.4 Results ............................................................... 174
6.5 Applications of the exact xc potentials ............................. 180
6.5.1 Constituent parts of the xc energy .............................. 180
6.5.2 Use of the potentials in fitting procedures .................... 183
6.6 Generalization of the Kohn-Sham scheme .......................... 189

7 Summary and future prospectives. ................................. 197

Ab initio studie van Dichtheidsfunctionaaltheorie via Greense func-
ties. .............................................................................. 203
1 Algemene situering en samenvatting van het onderzoek ............ 203
2 Het Greense functie formalisme ...................................... 206
3 Zelf-consistente oplossing van Dysons vergelijking voor gesloten schil
atomens ................................................................. 212
3.1 Numerieke oplossing van Dysons vergelijking tot op eerste
orde in de interactie .................................................. 213
3.2 Numerieke oplossing van Dysons vergelijking tot op tweede
orde in de interactie .................................................. 215
3.3 Het BAGEL schema .................................................. 217
3.4 Resultaten voor gesloten schil atomen ............................. 219
4 Zelf-consistente oplossing van Dysons vergelijking voor open schil atomen. ........................................ 222
   4.1 Veralgemeend formalisme en numeriek schema voor open schil atomen. ................................ 222
   4.2 Resultaten voor open schil atomen. ......................... 226
5 Dichtheidsfunctionaaltheorie. ........................................ 228
   5.1 De Hohenberg-Kohn theorema's. ............................ 228
   5.2 Het Kohn-Sham schema. ...................................... 232
6 Microscopische basis voor DFT via Greense functie technieken. ... 236
   6.1 Het inversie algoritme. ..................................... 237
   6.2 Resultaten van het inversie algoritme. .................... 239

A The atomic-units measurement system. 247
B Feynman rules in configuration-energy space. 249
C Positive definiteness of the Fock operator. 253
D Functional calculus. 255