

Electronic Structure of Crystalline Materials

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Chapter 1

Introduction

The present notes deal with the electronic structure of materials. They aim at the macroscopic electronic properties of metals, semiconductors and insulators and their relation to the microscopic degrees of freedom. The importance of the electronic properties stems from the fact that they influence a lot of different characteristics of matter as e.g. the electrical conductivity, the optical properties, the magnetic states, as well as the elastic properties. Knowledge of the electronic states thus provides a lot of information about a material.

Concentration on crystalline materials is mainly for historical reasons. From the very beginning solid state theory has put much emphasis on this form of condensed matter and provided a lot of experimental and theoretical tools adapted to it. As interest grew into other fields like amorphous systems, surfaces and interfaces these previously developed means were transferred with the necessary modifications.

Our goal is essentially twofold: First we want to learn about the concepts and methods to calculate at a microscopic level the electronic states, since they determine the macroscopic properties. We thus have to start at an atomistic level and use a quantum mechanical description. In principle, this “just” means to write down the Hamiltonian and solve the corresponding Schrödinger equation. Of course, in practice this problem is much too complicated for a closed solution and for this reason we call for simplifications. We are thus forced to use approximations in order to bring the full Hamiltonian into a tractable form. Fortunately, the development of solid state theory in the last century has placed at our disposal several such approximations, which nowadays build the basis for our current understanding. We mention, in particular:

1. The Born-Oppenheimer approximation, as proposed in 1927, enables an effective decoupling of the electronic and lattice degrees of freedom and, hence, allows to ignore the ionic dynamics in many cases, where only the electronic structure is of interest [20].
2. Of course, modern solid state physics has been benefiting much from Bloch’s theorem in 1929, which grew out of the early X-ray diffraction

studies and allowed to focus on a small unit cell with only few atoms instead of the full solid with of the order of 10^{23} atoms [18]. This way it was possible for the first time to cast the problem connected with the macroscopic crystal into a tractable form.

3. Hartree-Fock theory provided a set of eigenvalue equations for the single-particle states, which, though being quite complicated to solve, laid a sound basis for the electronic many-body problem and, hence, still influences further improvements of modern density functional theory [72, 54].
4. Considerable practical problems in solving Schrödinger's equations arise from the fact, that the valence electrons feel the strong potential near the nuclei and at the same time are able to pass through the solid across the weak potential between the nuclei. An efficient way to separate these two aspects was invented by Slater in 1937 by his famous “muffin-tin approximation”, which enabled for a piecewise determination of the wave function [151].
5. A much different approach to the same problem started out from the representation of the wave function in terms of orthogonalized plane waves, which laid ground for the pseudopotential method later on developed by Herring, Phillips and others [78, 138, 9].
6. The invention of density functional theory (DFT) and the local density approximation (LDA) in the mid sixties by Hohenberg, Kohn and Sham marked a milestone [80, 91], which has been described in numerous textbooks (see Sec. 9.1) and, providing the basis for modern materials science, has been honoured by the donation of the 1998 Nobel Prize in Chemistry to Walter Kohn.
7. The seventies witnessed such important steps as the concept of the so-called linear methods invented by Andersen [3, 4], which enabled for performing first principles calculations for unit cells of so far unaccessible size and, hence, furthered our understanding of materials considerably.
8. Finally, Car and Parrinello, by introducing first principles molecular dynamics, made the simultaneous *ab initio* investigation of electronic and ionic properties accessible [27].

All these approximations helped to bring the full Hamiltonian step by step into a form, which allowed for an efficient solution. While the approximations themselves are the subject of the first part of this book, we will turn in the second part in more detail to different calculational schemes. In doing so, we will especially concentrate on first principles approaches, which have established as an important branch of condensed matter physics and solid state chemistry in the past decades. In particular, the last ten years of this century have seen an increasing distribution of density functional based computational methods, which allow for a detailed understanding of electronic, magnetic and structural properties of condensed matter. Nowadays these methods can be easily applied

to rather complex systems and thus enable for the investigation of “real materials”. For this reason, band structure methods have left the realm of only a few specialists and have become a standard tool of materials science in university, research institutes and industry.

From the above list of approximations it is intuitively clear that they all, while simplifying the Hamiltonian, might exclude certain aspects of the physics behind it. This is indeed true and nowadays there is some effort to overcome previous approximations in order to study new phenomena. We already mentioned crystalline periodicity, which excludes investigation of amorphous solids, interfaces, defects, glass states, alloys, or clusters. Another example is the local density approximation (LDA) usually coming with density functional theory (DFT), which considerably underestimates optical band gaps and, hence, will have to be replaced by more elaborate methods in the future.

The second goal of the present work centers about the calculated results. We want to learn how they can be understood, interpreted and, last not least, be combined with experimental data, in order to further our insight into new materials.

Chapter 2

Reduction of the ionic degrees of freedom

2.1 The full Hamiltonian

Our understanding of condensed matter is based on the notion of a solid as being composed of heavy, positively charged ions and light, negatively charged valence electrons. It evolved at the end of the 19th and the beginning of the 20th century and built the backbone of Drude's theory of metals. The ions themselves consist of the nuclei of charge eZ , where e is the electronic charge and Z the atomic number, and the core electrons, which are tightly bound to the nuclei and, hence, do not contribute to metallic conductivity. This is different for the mobile valence electrons, which, in addition, are responsible for the cohesive and electrical properties of a solid.

Of course, the previous distinction between core and valence electrons is somewhat artificial. Let us assume, for instance, that we apply isotropic pressure to a solid. In this case the nuclei approach each other and the wave functions of the outer core electrons start to overlap. As a consequence, these electrons might escape from their parent nucleus and distribute in the solid, hence, take part in metallic conductivity just as the valence electrons already do in the uncompressed state. In order to avoid difficulties, we will thus keep the distinction between core and valence electrons rather flexible and use it only as a simplifying notation. In the same manner we will use the term ion for the nucleus with and without the core electrons depending on the context.

In order to describe the just sketched system of interacting ions and valence electrons we start out from the full Hamiltonian

$$H := H_{ion} + H_{el} + H_{ion-el} \quad , \quad (2.1.1)$$

where the three contributions are given by

$$H_{ion} := H_{ion,kin} + H_{ion-ion}$$

$$\begin{aligned}
& := \sum_{\mu} \left[-\frac{\hbar^2}{2M_{\mu}} \nabla_{\mu}^2 + \frac{1}{2} \sum_{\substack{\nu \\ \nu \neq \mu}} V_{ion-ion}(\mathbf{R}_{\mu} - \mathbf{R}_{\nu}) \right] \\
& := \sum_{\mu} \left[-\frac{\hbar^2}{2M_{\mu}} \nabla_{\mu}^2 + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\nu \\ \mu \neq \nu}} \frac{Z_{val,\mu} Z_{val,\nu}}{|\mathbf{R}_{\mu} - \mathbf{R}_{\nu}|} \right] , \quad (2.1.2)
\end{aligned}$$

$$\begin{aligned}
H_{el} & := H_{el,kin} + H_{el-el} \\
& := \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{j \\ j \neq i}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] , \quad (2.1.3)
\end{aligned}$$

$$\begin{aligned}
H_{ion-el} & := \sum_{\mu} \sum_i V_{ion-el}(\mathbf{r}_i - \mathbf{R}_{\mu}) \\
& := -\frac{e^2}{4\pi\epsilon_0} \sum_{\mu} \sum_i \frac{Z_{val,\mu}}{|\mathbf{R}_{\mu} - \mathbf{r}_i|} , \quad (2.1.4)
\end{aligned}$$

They account for the ionic and electronic subsystems as well as the coupling between these two. M_{μ} and m denote the masses of the ions and electrons, while \mathbf{R}_{μ} and \mathbf{r}_i are their positions. $Z_{val,\mu}$ is the number of valence electrons provided by the μ 'th ion, which is identical to the atomic number minus the number of core electrons of the ion. The respective first terms in Eqs. (2.1.2) and (2.1.3) contain the kinetic energy of the ions and electrons and the second terms comprise the pairwise interactions. Here we already specified that the electron-electron interaction like the ion-ion and ion-electron interaction are Coulombic.

For the following discussion it is useful to denote the full set of ionic and electronic coordinates, respectively as $\{\mathbf{R}_{\mu}\}$ and $\{\mathbf{r}_i\}$. Then we have from Eqs. (2.1.1) to (2.1.4)

$$\begin{aligned}
H & = H(\{\mathbf{r}_i, \mathbf{R}_{\mu}\}) \\
& = H_{ion}(\{\mathbf{R}_{\mu}\}) + H_{el}(\{\mathbf{r}_i\}) + H_{ion-el}(\{\mathbf{r}_i, \mathbf{R}_{\mu}\}) . \quad (2.1.5)
\end{aligned}$$

In the following two sections we will learn about approximations, which reduce especially the structural degrees of freedom of the above Hamiltonian. While the Born-Oppenheimer approximation deals with the kinetic energy term of the ionic Hamiltonian the assumption of a perfectly periodic crystal lattice aims at the ion-ion as well as the ion-electron interaction.

2.2 Born-Oppenheimer approximation

From the previous section it becomes clear that, while aiming at the calculation of the electronic states, we are, nevertheless, faced with the full problem posed by the Hamiltonian (2.1.1) containing both the ionic and electronic degrees of freedom. We thus have to solve Schrödinger's equation

$$H\Phi_{\gamma}(\{\mathbf{r}_i, \mathbf{R}_{\mu}\}) = \tilde{E}_{\gamma}(\{\mathbf{R}_{\mu}\})\Phi_{\gamma}(\{\mathbf{r}_i, \mathbf{R}_{\mu}\}) , \quad (2.2.1)$$

where γ labels the different eigenstates $\Phi_\gamma(\{\mathbf{r}_i, \mathbf{R}_\mu\})$. Eq. (2.2.1) poses a so far unsolvable problem and for this reason an approach for an effective decoupling of the electronic and ionic problems is called for. This is where the Born-Oppenheimer comes in [20]. From a physical point of view it is based on the fact that the electrons are much lighter than the nuclei. As a consequence, if the ions are not too far from their equilibrium positions the electrons move much faster than the nuclei and, hence, follow the ionic motion adiabatically. In other words, on the timescale of electronic motion the ions appear as being at fixed positions. At the same time the electronic distribution adds an extra term to the ion-ion potential.

A theoretical justification of the Born-Oppenheimer approximation can be achieved within the framework of perturbation theory where the small expansion parameter is the ratio of electronic and ionic masses. We will not follow this approach here but rather sketch some of the basic ideas while referring the more interested reader to the literature (see e.g. [176, 73, 24, 85]).

Since the electronic dynamics is much faster than the ionic motion, we assume, for the time being, the ions to be at fixed positions and solve Schrödinger's equation connected with the electronic problem, i.e.

$$\begin{aligned} H_{el,0}\psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) &:= \left(H_{el} + H_{ion-el} \right) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= E_{\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \quad , \end{aligned} \quad (2.2.2)$$

where $\bar{\alpha}$ labels different solutions of the electronic system, which, being eigenstates of $H_{el,0}$, are orthogonal and assumed to be normalized as well as real functions. The latter fact is a consequence of the real potential seen by the electrons. Note that the positions of the nuclei still enter the Hamiltonian $H_{el,0}$, the electronic wave functions $\psi_{\bar{\alpha}}$, and the energies $E_{\bar{\alpha}}$. However, they are just parameters here.

Since the solutions of Schrödinger's equation (2.2.2) form a complete set we are able to expand the solutions Φ_γ of Schrödinger's equation (2.2.1) connected with the full Hamiltonian (2.1.1) in the electronic states $\psi_{\bar{\alpha}}$, i.e.

$$\Phi_\gamma(\{\mathbf{r}_i, \mathbf{R}_\mu\}) = \sum_{\bar{\alpha}} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \quad . \quad (2.2.3)$$

Combining this expansion with Eq. (2.2.1) as well as with Schrödinger's equation (2.2.2) for the electronic problem we obtain

$$\begin{aligned} H\Phi_\gamma(\{\mathbf{r}_i, \mathbf{R}_\mu\}) &= (H_{ion} + H_{el,0}) \sum_{\bar{\alpha}} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= H_{ion} \sum_{\bar{\alpha}} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &\quad + \sum_{\bar{\alpha}} E_{\bar{\alpha}}(\{\mathbf{R}_\mu\}) \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &\stackrel{!}{=} \tilde{E}_\gamma(\{\mathbf{R}_\mu\}) \Phi_\gamma(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \quad . \end{aligned} \quad (2.2.4)$$

With the help of the identity

$$\begin{aligned}
& H_{ion} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\
&= \sum_{\mu} \left[-\frac{\hbar^2}{2M_{\mu}} \nabla_{\mu}^2 + \frac{1}{2} \sum_{\nu \neq \mu} V_{ion-ion}(\mathbf{R}_{\mu} - \mathbf{R}_{\nu}) \right] \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\
&= \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) H_{ion} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \\
&\quad - \sum_{\nu} \frac{\hbar^2}{2M_{\nu}} \left[\left(\nabla_{\nu}^2 \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \right) \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \right. \\
&\quad \quad \left. + 2 \nabla_{\nu} \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \cdot \nabla_{\nu} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \right] \quad (2.2.5)
\end{aligned}$$

this can be cast into the form

$$\begin{aligned}
& H \sum_{\bar{\alpha}} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\
&= \sum_{\bar{\alpha}} \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) H_{ion} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \\
&\quad - \sum_{\bar{\alpha}} \sum_{\nu} \frac{\hbar^2}{2M_{\nu}} \left[\left(\nabla_{\nu}^2 \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \right) \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \right. \\
&\quad \quad \left. + 2 \nabla_{\nu} \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \cdot \nabla_{\nu} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \right] \\
&\quad + \sum_{\bar{\alpha}} E_{\bar{\alpha}}(\{\mathbf{R}_\mu\}) \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \quad . \quad (2.2.6)
\end{aligned}$$

Next we multiply from the left with $\psi_{\bar{\alpha}'}(\{\mathbf{r}_i, \mathbf{R}_\mu\})$ and integrate out the electronic coordinates this leading to

$$\begin{aligned}
& \langle \psi_{\bar{\alpha}'}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) | H | \sum_{\bar{\alpha}} \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \rangle \\
&= \sum_{\bar{\alpha}} \left[\left(H_{ion} + E_{\bar{\alpha}}(\{\mathbf{R}_\mu\}) \right) \delta_{\bar{\alpha}'\bar{\alpha}} + C_{\bar{\alpha}'\bar{\alpha}}(\{\mathbf{R}_\mu\}) \right] \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \\
&= \tilde{E}_{\gamma}(\{\mathbf{R}_\mu\}) \varphi_{\gamma\bar{\alpha}'}(\{\mathbf{R}_\mu\}) \quad (2.2.7)
\end{aligned}$$

where the operator $C_{\bar{\alpha}'\bar{\alpha}}(\{\mathbf{R}_\mu\})$ is given by

$$\begin{aligned}
& C_{\bar{\alpha}'\bar{\alpha}}(\{\mathbf{R}_\mu\}) \\
&= - \int d^3\{\mathbf{r}_i\} \psi_{\bar{\alpha}'}^*(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\
&\quad \sum_{\nu} \frac{\hbar^2}{2M_{\nu}} \left[\left(\nabla_{\nu}^2 \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \right) + 2 \nabla_{\nu} \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \nabla_{\nu} \right] \quad . \quad (2.2.8)
\end{aligned}$$

In further evaluating this operator we follow the lines of Haug [73] and Ziman [175, 176]. We distinguish the non-diagonal from the diagonal terms and write for the second term

$$\begin{aligned} & \int d^3\{\mathbf{r}_i\} \psi_{\bar{\alpha}}^*(\{\mathbf{r}_i, \mathbf{R}_\mu\}) 2\nabla_\nu \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= \nabla_\nu \int d^3\{\mathbf{r}_i\} \psi_{\bar{\alpha}}^*(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) = \nabla_\nu Q_{el} = 0 \quad , \quad (2.2.9) \end{aligned}$$

where Q_{el} is the total electronic charge contained in the state $\psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\})$. Furthermore we note that the electrons are, at worst, tightly bound to their ions and, hence, the electronic wave functions depend on the electronic as well as ionic coordinates only via the differences $\mathbf{r}_j - \mathbf{R}_\nu$. We may thus write for the first term in Eq. (2.2.8)

$$\begin{aligned} & \int d^3\{\mathbf{r}_i\} \psi_{\bar{\alpha}}^*(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \frac{\hbar^2}{2M_\nu} \nabla_\nu^2 \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= \int d^3\{\mathbf{r}_i\} \psi_{\bar{\alpha}}^*(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \frac{\hbar^2}{2M_\nu} \nabla_j^2 \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= \frac{m}{M_\nu} \int d^3\{\mathbf{r}_i\} \psi_{\bar{\alpha}}^*(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \frac{\hbar^2}{2m} \nabla_j^2 \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \quad , \quad (2.2.10) \end{aligned}$$

which is just m/M_ν times the kinetic energy of the electrons. Since the ratio of the electronic and ionic masses is of the order of 10^{-3} to 10^{-4} this term is small compared to thermal energies and can thus be neglected.

In contrast, the non-diagonal elements of the operator $C_{\bar{\alpha}'\bar{\alpha}}(\{\mathbf{R}_\mu\})$ couple different ionic states $\varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\})$ and induce transitions between different electronic states as the ions move. Hence, these elements mediate the electron-phonon interaction. In the Born-Oppenheimer approximation the operator $C_{\bar{\alpha}'\bar{\alpha}}(\{\mathbf{R}_\mu\})$ is entirely ignored. Then we are left with only the diagonal terms of Eq. (2.2.7) and obtain

$$\left(H_{ion} + E_{\bar{\alpha}}(\{\mathbf{R}_\mu\}) \right) \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) = \tilde{E}_\gamma(\{\mathbf{R}_\mu\}) \varphi_{\gamma\bar{\alpha}}(\{\mathbf{R}_\mu\}) \quad , \quad (2.2.11)$$

which is just Schrödinger's equation for the ionic states. The Hamiltonian entering Eq. (2.2.11) thus results from the bare Hamiltonian H_{ion} of the ions as given by Eq. (2.1.2) by adding the "potential" $E_{\bar{\alpha}}(\{\mathbf{R}_\mu\})$, which is the total energy of the electronic systems as a function of the ionic positions. As the ions move this energy changes and adds an adiabatic contribution to the lattice energy. However, this extra term, although depending on the electronic wave functions $\psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\})$, is quite insensitive to the details of the electronic distribution since under normal conductivity conditions rearrangements of the electrons affect only states near the Fermi energy.

Finally, note that in Schrödinger's equation (2.2.2) for the electronic states the ions enter in their momentary positions. In contrast, in Eq. (2.2.11), which determines the ionic states, the average of the electronic distribution is considered. This reflects the abovementioned presence of different timescales of the ionic and electronic motion.

In summary, thanks to the Born-Oppenheimer approximation we are able to concentrate on the electronic problem posed by Eq. (2.2.2) while assuming the ions to stay at fixed positions. Nevertheless, even the Hamiltonian $H_{el,0}(\{\mathbf{r}_i, \mathbf{R}_\mu\})$ alone, which determines the electronic wave functions, still constitutes a difficult problem, which awaits further simplification.

Nevertheless, we should keep in mind that the Hamiltonian does not just reduce to $H_{el,0}(\{\mathbf{r}_i, \mathbf{R}_\mu\})$. Since the Born-Oppenheimer approximation affects only the kinetic energy of the ions we are still left with the ion-ion interaction, which must be included. Although we may regard $H_{ion-ion}$ just as a constant adding to the electronic energies its detailed form (2.1.2) becomes important whenever we have to perform lattice summations, which converge only due to the charge neutrality of each single unit cell. This point will become clearer when we deal with the homogeneous electron gas in Sec. 7.1. As a consequence of these considerations we are left with the Hamiltonian

$$H_0 := H_{ion-ion} + H_{el} + H_{ion-el} \quad , \quad (2.2.12)$$

with the single contributions given by Eqs. (2.1.2) to (2.1.4). This is the Hamiltonian, we will deal with in large parts of the remaining chapters.

2.3 Crystalline periodicity

The unique characteristic, which distinguishes crystals from all other modifications of matter, is discrete translational symmetry (see e.g. [10, 86] or any other textbook on solid state physics). It grew out of the early X-ray diffraction studies, which revealed that most materials condense into almost perfect periodic arrays at low temperatures. On the theoretical side translational symmetry led to the famous theorem formulated by Bloch, which allowed one to reduce the problem connected with the macroscopic crystal to that of a microscopic unit cell [18].

Although physically speaking the translational invariance of a crystal originates from a corresponding symmetry of the Hamiltonian the basic notions may, nevertheless, be understood from purely geometric considerations. From this rather mathematical point of view translational symmetry is equivalent to the existence of a lattice of points

$$\mathbf{R}_\mu = \sum_{i=1}^d n_{\mu i} \mathbf{a}_i \quad n_{\mu i} \text{ integer} \quad , \quad (2.3.1)$$

which fulfil the condition that the whole crystal (potential) looks the same when translated by a lattice vector \mathbf{R}_μ . d is the dimension of space and the vectors \mathbf{a}_i form a set of d linear independent vectors. For each μ the set of integers $n_{\mu i}, i = 1, \dots, d$ uniquely determines a lattice point. As is easily seen from the definition (2.3.1) the lattice points form an Abelian set with respect to addition, since the sum of two lattice points is again a lattice point irrespective of the order of summation. Moreover, a neutral element exists ($n_{\mu i} = 0$) as

well as an inverse element for each lattice point. We will come back to this property of the Bravais lattice in Sec. 2.5 when we derive the Bloch theorem.

The vectors \mathbf{a}_i entering Eq. (2.3.1) are called the primitive translations of a lattice. However, their determination is not unique. Each set of linear independent vectors, which allows to represent each lattice point in the form of Eq. (2.3.1), can be used as primitive translations. This is illustrated in Fig. 2.1 for a twodimensional lattice. The parallelepiped spanned by the vectors \mathbf{a}_i is

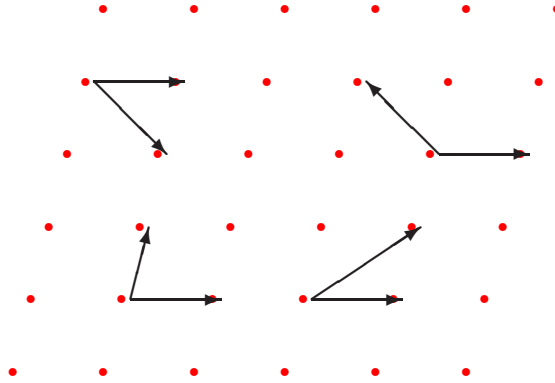


Figure 2.1: Primitive translations of a twodimensional lattice.

referred to as a primitive unit cell, which, like the primitive translations, is not uniquely determined. In general, each volume of space, which, when displaced by all vectors of the lattice, fills space completely without any overlap, is called a primitive cell. Again, this is illustrated by a twodimensional lattice in Fig. 2.2. A special choice, which is different from the simple parallelepiped, is

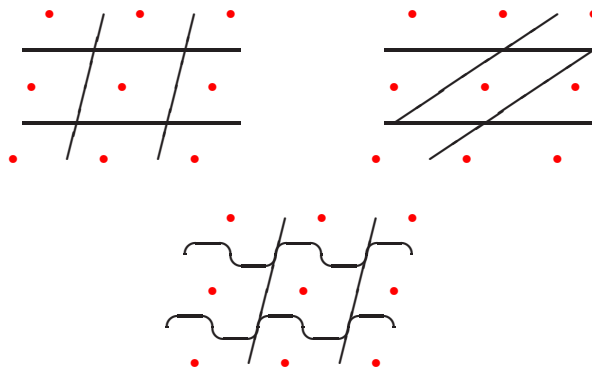


Figure 2.2: Primitive unit cells of a twodimensional lattice.

the so-called Wigner-Seitz cell. In addition to being a primitive unit cell, it displays the full symmetry of the lattice. The Wigner-Seitz cell is constructed

by selecting a certain lattice point as the origin and connecting the origin to the neighbouring points. Then all the planes, which bisect these lines bound the Wigner-Seitz cell. Again, this is illustrated by a twodimensional lattice in Fig. 2.3. Usually a fairly small number of such planes suffices to arrive

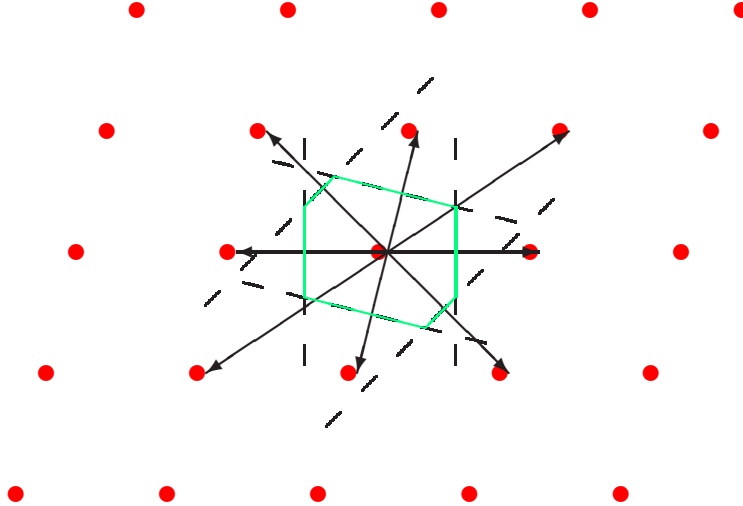


Figure 2.3: Wigner-Seitz cell of a twodimensional lattice.

at a closed surface; we only have to include all those $3^d - 1$ cells, which are direct neighbours of the original cell. The smallest possible cell constructed this way then defines the Wigner-Seitz cell. Below we will show examples for the Wigner-Seitz cells of the most common three-dimensional lattices.

In three dimensions there exist fourteen different lattices. They are called Bravais lattices in honour of A. Bravais, who was the first to give the correct number in 1845, and distinguished by additional symmetries beyond translational invariance as rotations or reflections, which transform the lattice to itself [10, 86, 24]. We list these lattices in Tab. 2.1, where we also give the restrictions of the lattice constants and the angles between the primitive translation vectors, which are a unique characteristic of each Bravais lattice.

We illustrate the previous notions with the three cubic (simple cubic (sc), face-centered cubic (fcc), and body-centered cubic (bcc)) as well as the hexagonal Bravais lattices. In case of the simple cubic lattice the primitive translations may be chosen along the Cartesian axes and both the Wigner-Seitz cell and the first Brillouin zone simply are cubes. The unit cell is shown in Fig. 2.4. More interesting are the other two cubic lattices. Their primitive translations read as

$$\mathbf{a}_1 = \frac{a}{2}(\mathbf{y} + \mathbf{z}), \quad \mathbf{a}_2 = \frac{a}{2}(\mathbf{z} + \mathbf{x}), \quad \mathbf{a}_3 = \frac{a}{2}(\mathbf{x} + \mathbf{y}) \quad (2.3.2)$$

for the fcc lattice and

$$\mathbf{a}_1 = \frac{a}{2}(-\mathbf{x} + \mathbf{y} + \mathbf{z}), \quad \mathbf{a}_2 = \frac{a}{2}(\mathbf{z} - \mathbf{y} + \mathbf{x}), \quad \mathbf{a}_3 = \frac{a}{2}(\mathbf{x} + \mathbf{y} - \mathbf{z}) \quad (2.3.3)$$

Bravais lattice		Lattice constants and angles
cubic	simple	$a = b = c$
	face-centered	$\alpha = \beta = \gamma = 90^\circ$
	body-centered	
tetragonal	simple	$a = b \neq c$
	centered	$\alpha = \beta = \gamma = 90^\circ$
orthorhombic	simple	$a \neq b \neq c$
	face-centered	$\alpha = \beta = \gamma = 90^\circ$
	body-centered	
	base-centered	
monoclinic	simple	$a \neq b \neq c$
	centered	$\alpha = \gamma = 90^\circ \neq \beta$
triclinic		$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
hexagonal		$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
trigonal		$a = b = c$ $\alpha = \beta = \gamma < 120^\circ$

Table 2.1: The fourteen three-dimensional Bravais lattices.

for the bcc lattice. Here a denotes the lattice constant and $\mathbf{x}, \mathbf{y}, \mathbf{z}$ are the Cartesian unit vectors. The corresponding unit cells are displayed in Figs. 2.5 and 2.6. We point out again that such crystal structure figures are meant only to visualize the symmetry of the full Hamiltonian as given by Eqs. (2.1.1) to (2.1.4). In order to stress this aspect we complement Fig. 2.5 with the corresponding crystal potential of copper as growing out of a density functional calculation plotted about one of the cube faces in Fig. 2.7. In Figs. 2.5 and 2.6 we have used the so-called conventional unit cell. It encloses the primitive cell but unravels its full symmetry. For this reason, the lattice points corresponding to the conventional cell are a subset of those of the original Bravais lattice. For the fcc and bcc lattice, the conventional unit cell is a simple cube, which comprises four and two primitive cells, respectively. A lot of elemental solids, which are listed in Tabs. 2.2 and 2.3, crystallize in the fcc and bcc lattices. Note that, following convention, the lattice constants given in these two tables are referred to the conventional simple cubic cell. In passing we point, in particular, to some peculiarities of the fcc lattice, namely the existence of corner-sharing octahedra formed e.g. by the atoms at the face centers of the cube. Another striking feature arises from the arrangement of the atoms in regular tetrahedra with edges of the same length as half of the face diagonal. Such tetrahedra

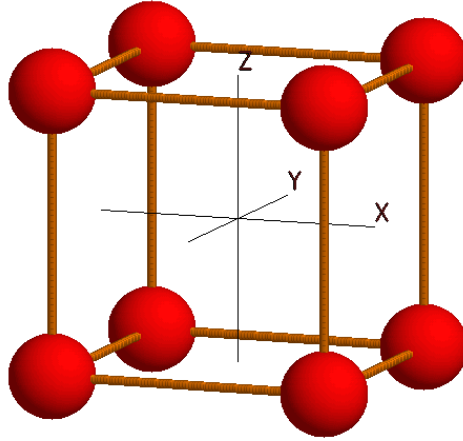


Figure 2.4: Simple cubic three-dimensional Bravais lattice.

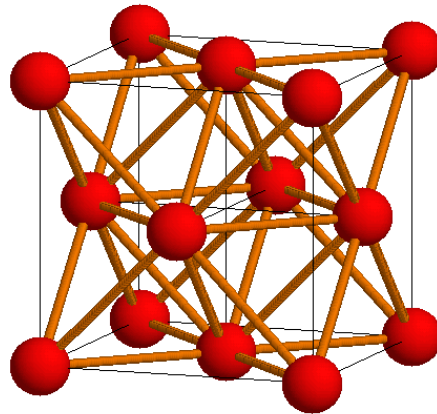


Figure 2.5: Face-centered cubic three-dimensional Bravais lattice.

might give rise to frustration effects, if e.g. the magnetic interactions between

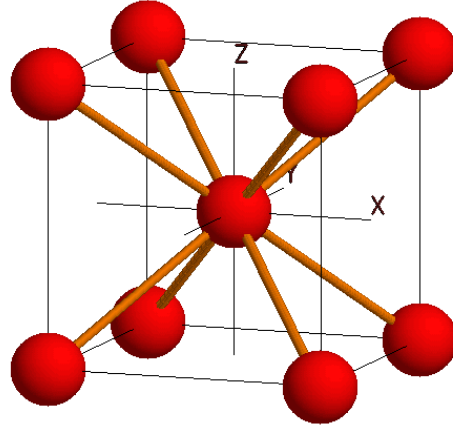


Figure 2.6: Body-centered cubic three-dimensional Bravais lattice.

Element	a (Å)	Element	a (Å)	Element	a (Å)
Ag	4.08	Cu	3.61	Pt	3.92
Al	4.05	Ir	3.84	Rh	3.80
Au	4.08	Ni	3.52	Sr	6.08
Ca	3.59	Pd	3.89		

Table 2.2: Elements with the face-centered cubic crystal structure.

spins located at the atomic sites suggest an antiferromagnetic alignment.

Element	a (Å)	Element	a (Å)	Element	a (Å)
Cr	2.89	Li	3.48 (4K)	Rb	5.70
Fe	2.87	Mo	3.15	Ta	3.30
K	5.32	Na	4.29	V	3.02
K	5.23 (5K)	Na	4.23 (5K)	W	3.17
Li	3.51	Nb	3.30		

Table 2.3: Elements with the body-centered cubic crystal structure.

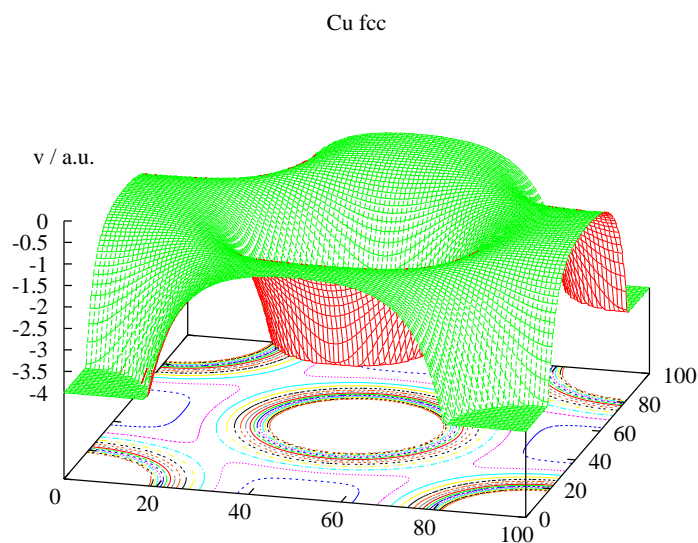


Figure 2.7: Single particle potential of fcc Cu as growing out of a density functional calculation.

In case of the hexagonal lattice the primitive translations are given by

$$\mathbf{a}_1 = -a\mathbf{y}, \quad \mathbf{a}_2 = a\left(\frac{\sqrt{3}}{2}\mathbf{x} + \frac{1}{2}\mathbf{y}\right), \quad \mathbf{a}_3 = c\mathbf{z} \quad , \quad (2.3.4)$$

in the notation of Bradley and Cracknell [22]. The unit cell of the hexagonal lattice is presented in Fig. 2.8 and in Tab. 2.4 we list a selection of elements

Element	a (Å)	c (Å)	c/a	Element	a (Å)	c (Å)	c/a
Be	2.29	3.58	1.567	Ru	2.71	4.28	1.582
Cd	2.98	5.62	1.886	Sc	3.31	5.27	1.594
Co	2.51	4.07	1.623	Ti	2.95	4.68	1.587
Hf	3.19	5.05	1.581	Tc	2.74	4.40	1.604
Mg	3.21	5.21	1.623	Y	3.65	5.73	1.571
Os	2.74	4.32	1.579	Zn	2.66	4.95	1.856
Re	2.76	4.46	1.615	Zr	3.23	5.15	1.593

Table 2.4: Elements with the hexagonal close-packed crystal structure.

crystallizing in the hexagonal Bravais lattice. Actually, most of these solids

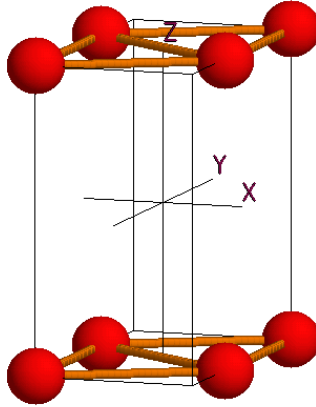


Figure 2.8: Hexagonal three-dimensional Bravais lattice.

do not form a simple hexagonal lattice but have unit cells, which comprise two atoms at different sites within the hexagonal cell. This results in the hexagonal close-packed (hcp) structure, which is shown in Fig. 2.9. It consists of hexagonal planes, which are vertically displaced by half of the lattice constant c . In addition, they are horizontally shifted such that an atom in one plane is at the center of the trigonal prism formed by the six neighbouring atoms in the planes below and above. To be concrete, if one of the atoms in the basal plane is located at the origin then the atom at the center of the prism is at

$$\mathbf{r} = \frac{1}{3}\mathbf{a}_1 - \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{a}_3 = -\frac{a}{2\sqrt{3}}\mathbf{x} - \frac{a}{2}\mathbf{y} + \frac{c}{2}\mathbf{z} \quad . \quad (2.3.5)$$

From this follows

$$|\mathbf{r}| = \sqrt{\frac{1}{3} + \frac{1}{4}\frac{c^2}{a^2}}a \quad . \quad (2.3.6)$$

If we require that three atoms in the basal plane and the central atom above form an ideal tetrahedron the distance $|\mathbf{r}|$ must be equal to the lattice constant a , which is fulfilled if $c/a = \sqrt{8/3} = 1.63299$. In this case the packing allows for an optimal filling of space. However, note that the hexagonal closed-packed structure does not form a Bravais lattice. This is easily seen from a fictitious lattice, where the inplane primitive translations \mathbf{a}_1 and \mathbf{a}_2 are those of the hexagonal lattice and the third primitive translation is chosen as the vector connecting atoms of two neighbouring planes. The result is shown in Fig. 2.10, which differs from Fig. 2.9 due to the different orientation of two next-

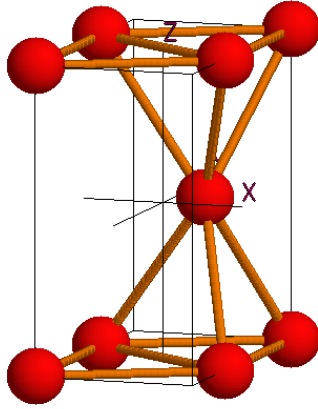


Figure 2.9: Hexagonal close-packed crystal structure.

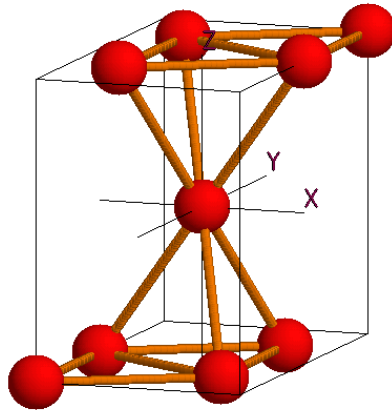


Figure 2.10: Fictitious close-packed crystal structure.

nearest layers. For this reason the hcp structure cannot be described as a

Bravais lattice without basis. As becomes obvious from Figs. 2.9 and 2.10 both structures can be distinguished by the different stacking of atoms. While the hcp structure follows an ABAB-type sequence, the stacking in Fig. 2.10 is of type ABCABC, since atoms in the second and third layer, respectively, are placed above different triangles formed by the first layer. Actually, this stacking gives rise to the fcc lattice, which is indeed shown in Fig. 2.10 with the z axis being the body diagonal of the cube. We recognize, in particular, the regular tetrahedra, which we discussed before. Still, the identity with the fcc lattice holds only for the ideal c/a value of 1.63299. In contrast, if we change c/a , hence, the separation of the layers or, viewed from within the cubic system, pull the unit cell along the body diagonal, we end up with the trigonal Bravais lattice, which may thus be regarded as a generalization of both the hexagonal and the fcc Bravais lattices.

As a matter of fact, the hcp structure is just one example of a crystal structure, where each primitive cell contains two atoms or more, which cannot be connected by a lattice vector of any Bravais lattice. This situation is called a lattice with a basis, where the latter is defined as the collection of atoms within a single primitive cell. Another example is the diamond structure, which we display in Fig. 2.11. It is characterized by a fcc Bravais lattice with two atoms

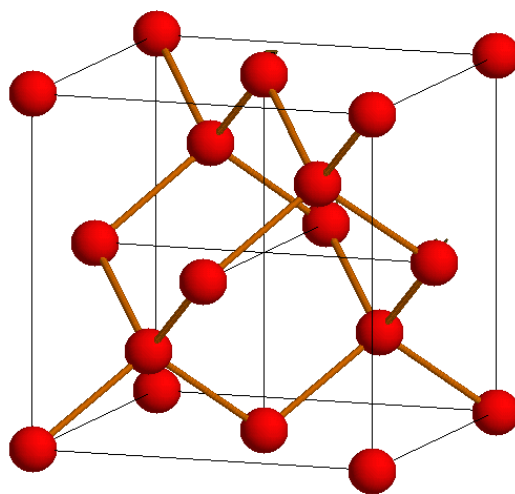


Figure 2.11: Diamond structure.

per primitive unit cell at points $(0, 0, 0)$ and $(1/4, 1/4, 1/4)a$. Elements crystallizing in this structure are listed in Tab. 2.5. A straightforward generalization of the diamond lattice arises, if we allow the two basis sites to be occupied by *different* atoms, this resulting in the zincblende structure, named after the

Element	a (Å)	Element	a (Å)
C	3.57	Si	5.43
Ge	5.66	α -Sn	6.49

Table 2.5: Elements with the diamond structure.

compound ZnS. It is displayed in Fig. 2.12 and in Tab. 2.6 we give a number of

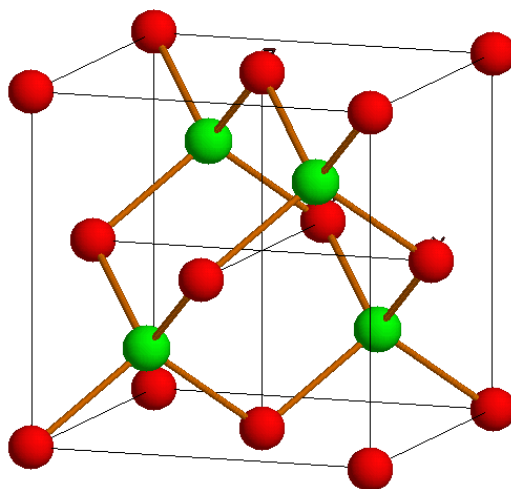


Figure 2.12: Zincblende structure.

compounds crystallizing in this structure. The list includes several transition metal halides as well as a lot of II-VI and III-V semiconductors.

Two prominent types of lattices for binary compounds arise as interpenetrating simple and face-centered cubic lattices with the origins displaced by half of the body diagonal. The results are the cesium chloride and the sodium chloride structure, respectively, which we display in Figs. 2.13 and 2.14, respectively. Typical compounds for both classes are listed in Tabs. 2.7 and 2.8. We finish this short survey by displaying in Fig. 2.15 the pyrite structure, which has a simple cubic lattice but a more complex arrangements of the atoms. This structure is adopted by several transition metal disulfides as e.g. FeS_2 and RuS_2 . While the transition metal atoms form an fcc lattice the sulfur atoms are placed at (x_S, x_S, x_S) . As a consequence, in order to completely specify this crystal structure we need, in addition, to the cubic lattice constant, the parameter x_S . For FeS_2 we have $x_S = 0.38484$. The pyrite crystal structure is best described in terms of the NaCl structure with the sublattices occupied by

Compound	a (Å)	Compound	a (Å)	Compound	a (Å)
CdS	5.82	AlP	5.45	CuF	4.26
CdTe	6.48	AlAs	5.62	CuCl	5.41
ZnS	5.41	AlSb	6.13	CuBr	5.69
ZnSe	5.67	GaP	5.45	CuI	6.04
ZnTe	6.09	GaAs	5.65	AgI	6.47
HgS	5.85	GaSb	6.12	BeS	4.85
HgSe	6.08	InP	5.87	BeSe	5.07
HgTe	6.43	InAs	6.04	BeTe	5.54
SiC	4.35	InSb	6.48		

Table 2.6: Binary compounds with the zincblende structure.

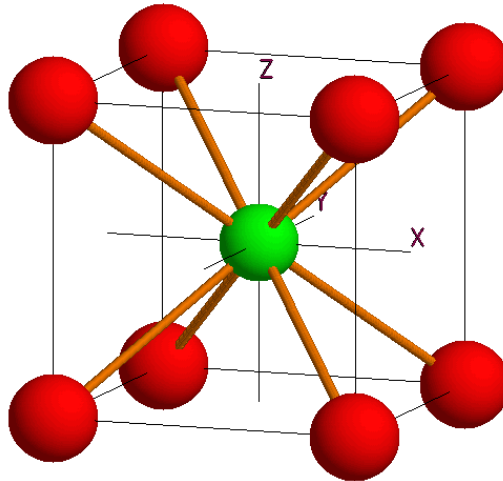


Figure 2.13: Cesium chloride structure.

iron atoms and the centers of gravity of sulfur atom pairs, respectively. These sulfur dumb-bells are oriented along the $\langle 111 \rangle$ axes. Being 2.161 \AA their bond length is still shorter than the Fe-S distance of 2.265 \AA . Whereas the sulfur atoms are tetrahedrally coordinated by one sulfur and three iron atoms the six nearest neighbour sulfur atoms at each iron site form slightly distorted octahedra. Due to the deformations of the octahedra the local symmetry at these sites is reduced from cubic (O_h) to trigonal (C_{3i}). The distorted FeS_6 octahedra are interlinked by common corners and, due to the formation of the $\langle 111 \rangle$

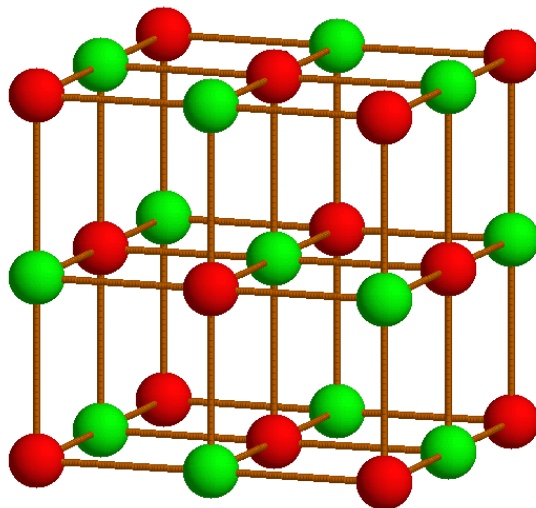


Figure 2.14: Sodium chloride structure.

Compound	a (Å)	Compound	a (Å)
CsCl	4.12	TlCl	3.83
CsBr	4.29	TlBr	3.97
CsI	4.57	TlI	4.20

Table 2.7: Binary compounds with the cesium chloride structure.

sulfur pairs, have rotated away from the cartesian axes by about 23° . For a two dimensional crystal the situation is sketched in Fig. 2.16. Obviously, the formation of the $\langle 111 \rangle$ sulfur pairs does not destroy the square planar coordination of the iron atoms. Instead, the squares built by the sulfur atoms just shrink and rotate. Since the orientation of the dumb-bells conforms with the cubic point group the underlying Bravais lattice is no longer face-centered but simple cubic and the unit cell comprises four formula units.

Again we complement Fig. 2.15 with the corresponding crystal potential as growing out of a density functional calculation plotted about one of the cube faces in Fig. 2.7. While the potential well at the middle of each edge arises from the iron atoms we observe the double potential well coming from a sulfur atom pair at the face center. In addition, a single sulfur potential well shows up near the corners in the foreground as well as the background.

Compound	a (Å)	Compound	a (Å)	Compound	a (Å)
LiF	4.02	RbF	5.64	CaO	4.81
LiCl	5.13	RbCl	6.58	CaS	5.69
LiBr	5.50	RbBr	6.85	CaSe	5.91
LiI	6.00	RbI	7.34	CaTe	6.34
NaF	4.62	CsF	6.01	SrO	5.16
NaCl	5.64	AgF	4.92	SrS	6.02
NaBr	5.97	AgCl	5.55	SrSe	6.23
NaI	6.47	AgBr	5.77	SrTe	6.47
KF	5.35	MgO	4.21	BaO	5.52
KCl	6.29	MgS	5.20	BaS	6.39
KBr	6.60	MgSe	5.45	BaSe	6.60
KI	7.07			BaTe	6.99

Table 2.8: Binary compounds with the sodium chloride structure.

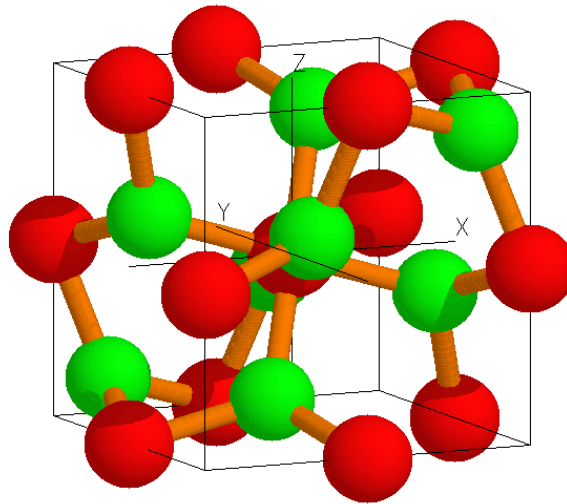


Figure 2.15: Pyrite structure. Transition metal and sulfur atoms are printed in red and green, respectively.

2.4 The reciprocal lattice

We complement the basic definition (2.3.1) of the Bravais lattice as a set of discrete, equally spaced *points* by an alternative representation in terms of

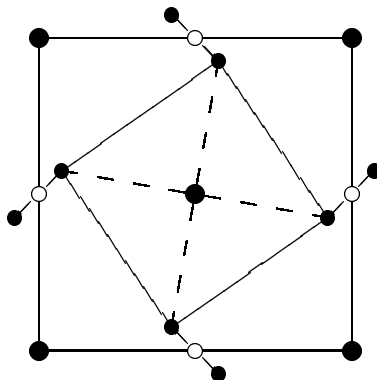


Figure 2.16: Twodimensional analogue of the pyrite structure. Big and small filled circles designate iron and sulfur atoms, respectively. Small open circles mark the ideal positions conforming with the rocksalt structure.

FeS₂ sc

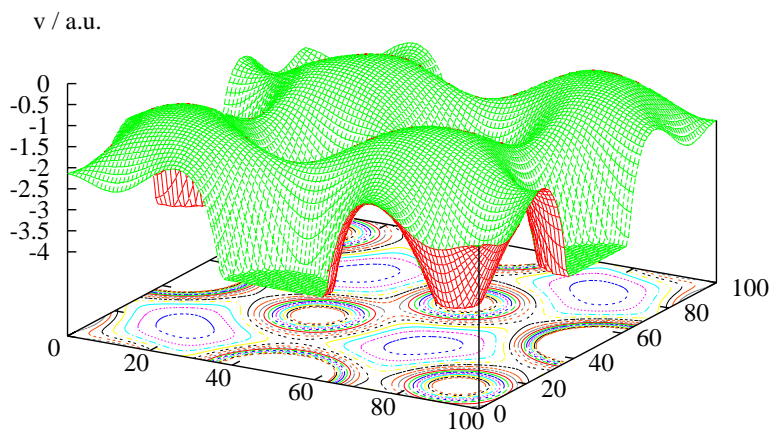


Figure 2.17: Single particle potential of fcc FeS₂ as growing out of a density functional calculation.

lattice planes. For a given Bravais lattice a lattice plane is defined by three noncollinear lattice points. Due to the definition of the Bravais lattice each plane contains infinitely many points and to each such lattice plane there exist infinitely many parallel planes. Together these parallel planes form a *family of lattice planes*. Eventually, each point of the Bravais lattice may be uniquely

assigned to one of the planes of a family.

Obviously, each Bravais lattice gives rise to many families of lattice planes. However, each such family is uniquely determined by the distance d_ν between the planes and the unit vector \mathbf{u}_ν perpendicular to the planes. Formally, each family is then characterized by the Hessian equation, which is a condition for any vector \mathbf{r} lying on the ν 's plane,

$$\mathbf{u}_\nu \cdot \mathbf{r} - Nd_\nu = 0, \quad \text{for } N = 0, \pm 1, \pm 2, \dots \quad (2.4.1)$$

In particular, this equation holds for all points \mathbf{R}_μ of the Bravais lattice, which lie in the respective plane. Combining now the two characteristics of a family, d_ν and \mathbf{u}_ν , into a single vector,

$$\mathbf{K}_\nu = \frac{2\pi}{d_\nu} \mathbf{u}_\nu \quad (2.4.2)$$

we rewrite the condition (2.4.1) specifically for a lattice vector \mathbf{R}_μ as

$$\mathbf{K}_\nu \cdot \mathbf{R}_\mu = 2\pi N \quad (2.4.3)$$

Obviously, the vectors \mathbf{K}_ν are wave vectors of plane waves $e^{i\mathbf{K}_\nu \cdot \mathbf{r}}$ propagating along \mathbf{u}_ν with wavelength $\lambda = 2\pi/|\mathbf{K}_\nu| = d_\nu$. As a consequence, by proceeding by on lattice vector the plane wave reproduces itself. Hence, the vectors of the reciprocal lattice must fulfil the condition

$$e^{i\mathbf{K}_\nu \cdot (\mathbf{r} + \mathbf{R}_\mu)} = e^{i\mathbf{K}_\nu \cdot \mathbf{r}} \quad (2.4.4)$$

for all vectors \mathbf{r} and all lattice vectors \mathbf{R}_μ . From this we have

$$e^{i\mathbf{K}_\nu \cdot \mathbf{R}_\mu} \stackrel{!}{=} 1 \quad (2.4.5)$$

which is equivalent to equation (2.4.3).

Still, we want to prove that the wave vectors \mathbf{K}_ν themselves form a Bravais lattice. Of course, we may conclude from the symmetry of equations (2.4.3) and (2.4.5) with respect to exchange of \mathbf{K}_ν and \mathbf{R}_μ that the wave vectors also form a Bravais lattice. We will call this lattice the reciprocal lattice, since, according to equation (2.4.2), these vectors have the dimension of an inverse length. Nevertheless, we prefer to deduce the property of a lattice more directly. Since, according to the definition (2.3.1), the lattice points \mathbf{R}_μ are linear combinations of the primitive translations, equation (2.4.3) holds especially for the latter,

$$\mathbf{K}_\nu \cdot \mathbf{a}_i = 2\pi N, \quad \text{for } N = 0, \pm 1, \pm 2, \dots \quad \text{and } i = 1, d \quad (2.4.6)$$

Furthermore, for each \mathbf{a}_i there exists one particular wave vector with $N = 1$, i.e.

$$\mathbf{b}_i \cdot \mathbf{a}_i = 2\pi, \quad \text{for } i = 1, d \quad (2.4.7)$$

Being wave vectors the \mathbf{b}_i must be perpendicular to a family of lattice planes. In particular, they must be perpendicular to those lattice planes, which are

spanned by the respective other two primitive translations, this giving rise to the general condition

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \cdot \delta_{ij} \quad , \quad (2.4.8)$$

which is fulfilled if the primitive wave vectors \mathbf{b}_i are defined by

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)} \quad , \quad i, j, k \text{ cyclic} \quad , \quad (2.4.9)$$

where

$$\Omega_{UC} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \quad (2.4.10)$$

is the volume of the unit cell. Finally, in order that any wave vector obeys equation (2.4.6) it must be given by

$$\mathbf{K}_\nu = \sum_{i=1}^d m_{\nu i} \mathbf{b}_i \quad , \quad (2.4.11)$$

which, in the same manner as equation (2.3.1) defines a Bravais lattice, the reciprocal lattice. Combining equations (2.3.1) and (2.4.11) we arrive at

$$\mathbf{R}_\mu \mathbf{K}_\nu = 2\pi \cdot \sum_{i=1}^d n_{\mu i} m_{\nu i} \quad , \quad (2.4.12)$$

which again is just a different formulation of equation (2.4.3).

In the same manner as for the real space lattice there also exist primitive unit cells for the reciprocal lattice. In addition, again a fully symmetric primitive unit cell can be constructed. In reciprocal space this Wigner-Seitz cell is called the first Brillouin zone.

Again, we illustrate the previous definitions with the three cubic as well as the hexagonal Bravais lattices. In case of the simple cubic lattice the primitive translations of the reciprocal lattice are just parallel to those of the real space lattice with the reciprocal vectors scaling as $2\pi/a$. In contrast, the reciprocal primitive translations of the fcc and bcc lattice are calculated from Eq. (2.4.9) as translations as

$$\mathbf{b}_1 = \frac{2\pi}{a}(-\mathbf{x} + \mathbf{y} + \mathbf{z}), \quad \mathbf{b}_2 = \frac{2\pi}{a}(\mathbf{z} - \mathbf{y} + \mathbf{x}), \quad \mathbf{b}_3 = \frac{2\pi}{a}(\mathbf{x} + \mathbf{y} - \mathbf{z}) \quad (2.4.13)$$

for the fcc lattice and

$$\mathbf{b}_1 = \frac{2\pi}{a}(\mathbf{y} + \mathbf{z}), \quad \mathbf{b}_2 = \frac{2\pi}{a}(\mathbf{z} + \mathbf{x}), \quad \mathbf{b}_3 = \frac{2\pi}{a}(\mathbf{x} + \mathbf{y}) \quad (2.4.14)$$

for the bcc lattice. Hence, except for a scale factor the reciprocal of the fcc lattice is just the bcc lattice and vice versa. As a consequence, the Wigner-Seitz cell of each of these two lattices is identical to the first Brillouin zone of the respective other lattice. This is why we did not display the former ones but now give the Brillouin zones in Figs. 2.18 and 2.19. There we have, in

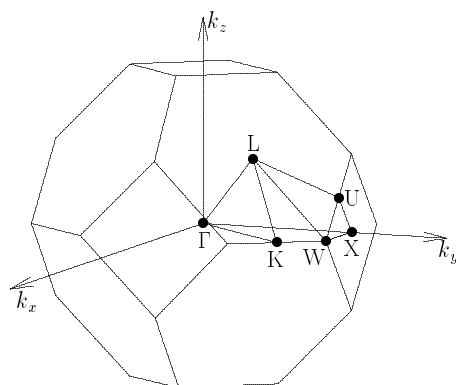


Figure 2.18: First Brillouin zone of the fcc lattice.

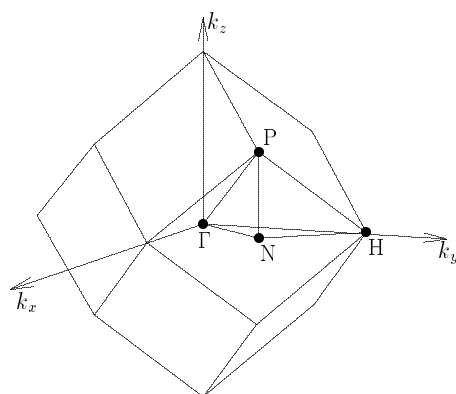


Figure 2.19: First Brillouin zone of the bcc lattice.

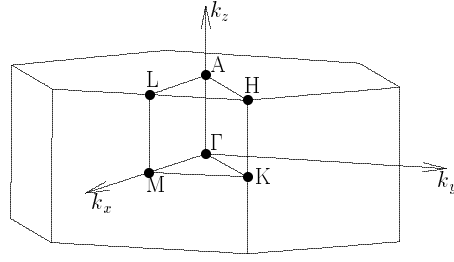


Figure 2.20: First Brillouin zone of the hexagonal lattice.

addition, highlighted some special \mathbf{k} points, which are labelled according to the convention first introduced by Bouckaert *et al.* [21] (see also [22]) and which will be discussed in more detail below.

In case of the hexagonal lattice the reciprocal space primitive translations are readily written down as

$$\mathbf{b}_1 = \frac{2\pi}{a} \left(\frac{1}{\sqrt{3}} \mathbf{x} - \mathbf{y} \right), \quad \mathbf{b}_2 = \frac{2\pi}{a} \frac{2}{\sqrt{3}} \mathbf{x}, \quad \mathbf{b}_3 = \frac{2\pi}{c} \mathbf{z} \quad (2.4.15)$$

and the first Brillouin zone of the hexagonal lattice is given in Fig. 2.20.

2.5 Bloch's theorem

We turn back to the physics underlying crystal symmetry and discuss its consequences on the electronic states. This leads to Bloch's theorem. As already pointed out in the previous section crystal symmetry results from a corresponding symmetry of the Hamiltonian

$$H(\mathbf{r} + \mathbf{R}_\mu) = H(\mathbf{r}) \quad . \quad (2.5.1)$$

In other words, the Hamiltonian is invariant under a translation by an arbitrary lattice vector and thus it commutes with all the translation operators,

$$[H, T_{\mathbf{R}_\mu}]_- = 0 \quad \forall \mu \quad , \quad (2.5.2)$$

which are defined by the way they act onto a function in space,

$$T_{\mathbf{R}_\mu} f(\mathbf{r}) := f(\mathbf{r} + \mathbf{R}_\mu) \quad . \quad (2.5.3)$$

The basic properties of the translation operators are easily derived. Obviously, successive translations by the lattice vectors \mathbf{R}_μ and \mathbf{R}_ν in either order are equivalent to the single translation by $\mathbf{R}_\mu + \mathbf{R}_\nu$, i.e.

$$T_{\mathbf{R}_\mu} T_{\mathbf{R}_\nu} = T_{\mathbf{R}_\nu} T_{\mathbf{R}_\mu} = T_{\mathbf{R}_\mu + \mathbf{R}_\nu} \quad . \quad (2.5.4)$$

Especially for $\mathbf{R}_\nu = -\mathbf{R}_\mu$ we obtain

$$T_{\mathbf{R}_\mu} T_{-\mathbf{R}_\mu} = T_{-\mathbf{R}_\mu} T_{\mathbf{R}_\mu} = T_{\mathbf{0}} = \mathcal{I} \quad (2.5.5)$$

where \mathcal{I} is the unity operator. In particular, Eq. (2.5.5) serves as a definition of the inverse translation operator. We thus arrive at the conclusion that all translation operators form an Abelian group. Actually, we had assigned this property already to the Bravais lattice points \mathbf{R}_μ . However, we point out that the translation $T_{\mathbf{R}_\mu}$ by a lattice vector is equivalent to the lattice point itself, so the difference is rather artificial.

Since the translation operators commute with the Hamiltonian both have the same system of eigenfunctions and we are thus able to write

$$T_{\mathbf{R}_\mu} \psi_n(\mathbf{r}) = \lambda_\mu \psi_n(\mathbf{r}) \quad (2.5.6)$$

where the $\psi_n(\mathbf{r})$ are the eigenfunctions of the Hamiltonian,

$$H(\mathbf{r}) \psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r}) \quad (2.5.7)$$

and n labels different eigenfunctions. Still we have to deduce the eigenvalues λ_μ of the translation operators. To this end we again employ crystal translational symmetry, which requires that the results of any measurement are unaffected by a translation. For this reason, the square of the norm of the wave function must be invariant and the eigenvalues λ_μ of the translation operators must be complex and of modulus 1. Hence

$$\lambda_\mu = e^{i\Theta_\mu} \quad . \quad (2.5.8)$$

Combining Eqs. (2.5.4), (2.5.6) and (2.5.8) we obtain the identity

$$e^{i\Theta_\mu} e^{i\Theta_\nu} = e^{i(\Theta_\mu + \Theta_\nu)} \quad , \quad (2.5.9)$$

which is fulfilled if

$$\Theta_\mu = \mathbf{k} \mathbf{R}_\mu \quad (2.5.10)$$

with the vector \mathbf{k} as yet unspecified. Combining this with Eqs. (2.5.3), (2.5.6) and (2.5.8) we finally arrive at Bloch's theorem

$$\psi_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}_\mu) = e^{i\mathbf{k} \mathbf{R}_\mu} \psi_{n\mathbf{k}}(\mathbf{r}) \quad (2.5.11)$$

where the function $\psi_{n\mathbf{k}}(\mathbf{r})$ is called a Bloch function [18]. Note that we have used the \mathbf{k} vector as an additional label.

Bloch's theorem sometimes is written in an alternative form, which arises from inserting

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (2.5.12)$$

into Eq. (2.5.11). This results in

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}_\mu) = u_{n\mathbf{k}}(\mathbf{r}) \quad . \quad (2.5.13)$$

Thus, according to Bloch's theorem the wave function can be written as the product of a phase factor and a function $u_{n\mathbf{k}}(\mathbf{r})$, which has the periodicity of the lattice.

Obviously, the vector \mathbf{k} has the dimension of an inverse length and we may thus assign it to reciprocal space. Moreover, it is possible to consider only those \mathbf{k} vectors, which belong to the first Brillouin zone. To see this we start from two vectors \mathbf{k} and \mathbf{k}' , which are separated by a lattice vector \mathbf{K}_ν ,

$$\mathbf{k}' = \mathbf{k} + \mathbf{K}_\nu \quad . \quad (2.5.14)$$

Due to the identity (2.4.5) wave functions labelled with vectors \mathbf{k} and \mathbf{k}' belong to the same eigenspace, i.e.

$$T_{\mathbf{R}_\mu} \psi_{n\mathbf{k}'}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{R}_\mu} \psi_{n\mathbf{k}'}(\mathbf{r}) \quad (2.5.15)$$

and

$$T_{\mathbf{R}_\mu} \psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{R}_\mu} \psi_{n\mathbf{k}}(\mathbf{r}) \quad . \quad (2.5.16)$$

Since the translation operators form an Abelian group giving rise to only one-dimensional representations, hence, one-dimensional eigenspaces, the wave functions entering equations (2.5.15) and (2.5.16) must be identical. The same holds for the eigenvalues of the Hamiltonian and we note the result

$$\psi_{n\mathbf{k}+\mathbf{K}_\nu}(\mathbf{r}) = \psi_{n\mathbf{k}}(\mathbf{r}) \quad (2.5.17)$$

and

$$\varepsilon_{n\mathbf{k}+\mathbf{K}_\nu} = \varepsilon_{n\mathbf{k}} \quad . \quad (2.5.18)$$

In the previous equations we have already labelled the different eigenfunctions of the Hamiltonian as arising from (2.5.7) by n . Due to the use of periodic boundary conditions the periodic part of the wave function, which is given by Eq. (2.5.13), needs to be specified only within a single unit cell. For this reason, Schrödinger's equation has to be solved only in a finite volume and we expect a discrete spectrum of eigenvalues, distinguished by the label n .

Of course, crystals can possess more than translational symmetry and indeed most crystals realized in nature do. The operations connected with the additional symmetries are rotations and reflections and like the translations they form groups. These groups are called point groups since rotations and reflections (which can be viewed as rotations followed by inversion) are all taken about a fixed center. In the same manner as in the case of the translations point group symmetries arise from an underlying symmetry of the Hamiltonian and thus the corresponding operators commute with H .

Finally, the point group operations may be combined with fractional translations, which are translations by non-lattice vectors. This gives rise to screw axes and glide planes. Altogether the fourteen Bravais lattices and 32 point groups then lead to the 230 space groups. Each space group is distinguished by the way the atoms are arranged within the primitive cell. Since a more detailed discussion of the subject is beyond the scope of this chapter we refer the interested reader to the literature (see e.g. Refs. [95, 23, 96, 22, 106]).

Obviously, rotations, reflections and fractional translations lead to planes, lines and points both in real and reciprocal space, which are invariant under all

these operations. In \mathbf{k} space they confine, in particular, the irreducible wedge of the first Brillouin zone, which, by applying all allowed space group operations, fills the whole first Brillouin zone without overlap. For the evaluation of \mathbf{k} space integrals it is thus sufficient to calculate the wave functions $\psi_{n\mathbf{k}}(\mathbf{r})$ and eigenvalues $\varepsilon_{n\mathbf{k}}$ only in the irreducible wedge. As concerns the representation and interpretation of results it has become customary to plot all the $\varepsilon_{n\mathbf{k}}$ along some of the abovementioned symmetry lines connecting the high-symmetry points (which we have already indicated in Figs. 2.18 to 2.20). This is what is usually termed the band structure.

2.6 Born-von Kármán boundary conditions

With Bloch's theorem at hand we have a first glimpse at the solutions of Schrödinger's equation for a crystalline solid. However, in order to completely specify the wave function, we will need boundary conditions. This includes specifying the shape of the crystal. Nevertheless, as long as we are not interested in surface properties, the particular choice of the boundary conditions must not alter the result and, hence, must not be important. First of all, we thus assume that the crystal has the shape of a parallelepiped with axes parallel to the primitive translation vectors of the Bravais lattice. A simple choice for the boundary condition would be to require the wave function to vanish at the surface of the parallelepiped, which leads to standing wave solutions. Yet, transport properties rather call for propagating waves. For this reason, we follow convention and choose Born-von Kármán or periodic boundary conditions,

$$\psi_{n\mathbf{k}}(\mathbf{r} + N_i \mathbf{a}_i) = \psi_{n\mathbf{k}}(\mathbf{r}), \quad i = 1, 2, 3 \quad . \quad (2.6.1)$$

The \mathbf{a}_i denote the primitive translations and the N_i are integers, where $N_{UC} = N_1 \cdot N_2 \cdot N_3$ is the total number of primitive cells in the crystal. Applying Bloch's theorem (2.5.11) to the boundary condition (2.6.1) we find that

$$e^{iN_i \mathbf{k} \mathbf{a}_i} = 1 \quad . \quad (2.6.2)$$

Since any vector \mathbf{k} in reciprocal space can be written as

$$\mathbf{k} = \sum_{i=1}^d x_{\mathbf{k}i} \mathbf{b}_i \quad (2.6.3)$$

Eqs. (2.4.11) and (2.6.2) imply

$$x_{\mathbf{k}i} = \frac{m_{\mathbf{k}i}}{N_i} \quad , \quad (2.6.4)$$

where $m_{\mathbf{k}i}$ is an integer, or else

$$\mathbf{k} = \sum_{i=1}^d \frac{m_{\mathbf{k}i}}{N_i} \mathbf{b}_i \quad . \quad (2.6.5)$$

As a consequence, all allowed \mathbf{k} vectors lie on an equidistant grid in the reciprocal primitive cell, which becomes infinitesimally fine for $N_{UC} \rightarrow \infty$. It follows from Eq. (2.6.5) that the volume $\Omega_{\mathbf{k}}$ per \mathbf{k} point is just the volume of the reciprocal unit cell

$$\Omega_{BZ} := \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3) = \frac{(2\pi)^3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} =: \frac{(2\pi)^3}{\Omega_{UC}} \quad (2.6.6)$$

divided by the number N_{UC} of micro-parallelepipeds, i.e.

$$\Omega_{\mathbf{k}} = \frac{\Omega_{BZ}}{N_{UC}} = \frac{(2\pi)^3}{N_{UC} \cdot \Omega_{UC}} = \frac{(2\pi)^3}{\Omega} \quad , \quad (2.6.7)$$

where Ω denotes all space.

2.7 Brillouin zone integration

As a matter of fact, a lot of physical quantities arise as integrals over the Brillouin zone of the general form

$$I_A(E) = \frac{1}{\Omega_{BZ}} \sum_n \int_{\Omega_{BZ}} d^3\mathbf{k} A_{n\mathbf{k}} \delta(E - \varepsilon_{n\mathbf{k}}) \quad . \quad (2.7.1)$$

where the weights $A_{n\mathbf{k}}$ are associated with the electronic states $\psi_{n\mathbf{k}}(\mathbf{r})$ and $\delta(x)$ is Dirac's δ distribution. Quite often the quantities $A_{n\mathbf{k}}$ entering the integral (2.7.1) depend on the band index n and wave vector \mathbf{k} only via the eigenvalues $\varepsilon_{n\mathbf{k}}$ of the Hamiltonian,

$$A_{n\mathbf{k}} = \tilde{A}_n(\varepsilon_{n\mathbf{k}}) \quad , \quad (2.7.2)$$

in which case Eq. (2.7.1) reduces to

$$I_A(E) = \frac{1}{\Omega_{BZ}} \sum_n \tilde{A}_n(E) \int_{\Omega_{BZ}} d^3\mathbf{k} \delta(E - \varepsilon_{n\mathbf{k}}) \quad . \quad (2.7.3)$$

In particular, for $A_{n\mathbf{k}} = 1$, we arrive at the definition of the density of states for the n th band by

$$\rho_n(E) := \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d^3\mathbf{k} \delta(E - \varepsilon_{n\mathbf{k}}) \quad , \quad (2.7.4)$$

which allows to write the integral (2.7.3) as

$$I_A(E) = \sum_n \tilde{A}_n(E) \rho_n(E) \quad . \quad (2.7.5)$$

According to Eq. (2.7.4) the density of states $\rho_n(E)$ thus denotes just that fraction of the Brillouin zone, which comprises the states with energy E .

In practice, we will replace the integral (2.7.1) by a weighted sum over a finite number of \mathbf{k} points of the reciprocal unit cell,

$$I_A(E) = \frac{1}{N_{UC}} \sum_{n\mathbf{k}} A_{n\mathbf{k}} \delta(E - \varepsilon_{n\mathbf{k}}) \quad , \quad (2.7.6)$$

Of course, in the limit of infinite N_{UC} this sum turns into an over the first Brillouin zone according to

$$\Omega_{\mathbf{k}} \sum_{\mathbf{k}} \rightarrow \int_{\Omega_{BZ}} d^3\mathbf{k} \quad . \quad (2.7.7)$$

Using Eq. (2.7.6) we thus write for the density of states.

$$\rho_n(E) = \frac{1}{\Omega_{BZ}} \Omega_{\mathbf{k}} \sum_{\mathbf{k}} \delta(E - \varepsilon_{n\mathbf{k}}) \quad . \quad (2.7.8)$$

A different formulation of the density of states arises from representing the volume of integration as a sequence of shells of thickness dE ,

$$\rho_n(E)dE = \frac{1}{\Omega_{BZ}} \int_{E \dots E+dE} d\mathbf{k}_{\perp} \int_{S_n(E)} dS \mathbf{u} \delta(E - \varepsilon_{n\mathbf{k}}) \quad , \quad (2.7.9)$$

where

$$\mathbf{u} = \frac{\nabla \varepsilon_{n\mathbf{k}}}{|\nabla \varepsilon_{n\mathbf{k}}|} \quad (2.7.10)$$

is the unity vector perpendicular to the surface element. Since

$$dE = \nabla \varepsilon_{n\mathbf{k}} \cdot d\mathbf{k}_{\perp} \quad (2.7.11)$$

we obtain

$$\rho_n(E)dE := \frac{1}{\Omega_{BZ}} \int_{E \dots E+dE} dE \int_{S_n(E)} dS \frac{1}{|\nabla \varepsilon_{n\mathbf{k}}|} \delta(E - \varepsilon_{n\mathbf{k}}) \quad , \quad (2.7.12)$$

hence, the result

$$\rho_n(E) := \frac{1}{\Omega_{BZ}} \int_{S_n(E)} dS \frac{1}{|\nabla \varepsilon_{n\mathbf{k}}|} \delta(E - \varepsilon_{n\mathbf{k}}) \quad , \quad (2.7.13)$$

which establishes an explicit connection between the band structure and the density of states. A general feature of the density of states can be easily derived. Since according to Eq. (2.5.18) the electronic states are periodic functions in \mathbf{k} space, bounded above and below for each band n , there must be points within each cell, where the gradient $|\nabla \varepsilon_{n\mathbf{k}}|$ vanishes. Although at such points the integrand in Eq. (2.7.13) diverges, it can be shown that in three dimensions the integral itself does not. In contrast, these so-called van Hove singularities are integrable and give rise to kinks in the density of states curves.

The actual calculation of densities of states is not a trivial task and a lot of work has been done in order to develop both accurate and efficient schemes. It includes the selection of so-called special points, which, when used for summations as in Eq. (2.7.2), approximate the Brillouin zone integral very well [13, 32, 116], as well as schemes for the efficient evaluation of integrals from the $A_{n\mathbf{k}}$ calculated at a finite set of points. For electronic structure calculations most often used methods are sampling schemes as well as the linear tetrahedron method (see for example [115, 19] and references therein).

Chapter 3

The Sommerfeld theory of metals

3.1 The Sommerfeld model

We illustrate the previous notions with the most simple quantum mechanical model of the electronic states in a crystal, the Sommerfeld theory of metals. It is founded on two basic assumptions:

1. In the *free electron approximation* the potential due to the ions is completely ignored and replaced by a positively charged constant background.
2. In the *independent electron approximation* the electron-electron interaction is completely ignored.

While accepting these assumptions for the time being we postpone a more detailed discussion of their motivations, advantages and drawbacks to Secs. 7.1 and 4.1.

We are then left with only the kinetic energy contribution to the Hamiltonian (2.1.1) to (2.1.4) and the single particle states must obey Laplace's equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \varepsilon \right] \chi(\mathbf{r}) = 0 \quad , \quad (3.1.1)$$

which is solved by normalized plane waves

$$\chi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_{UC}\Omega_{UC}}} e^{i\mathbf{k}\mathbf{r}} = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\mathbf{r}} \quad (3.1.2)$$

with momentum

$$\mathbf{p} = \hbar\mathbf{k} \quad (3.1.3)$$

and energy

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad . \quad (3.1.4)$$

According to Eq. (2.5.18) the energy dispersion relation $\varepsilon_{\mathbf{k}}$ is periodic in \mathbf{k} space. We thus have an infinite number of energy parabolas of the form (3.1.4), each of which is centered in a different cell of reciprocal space. Within each cell all these parabolas intersect and give rise to a complicated looking pattern of electronic bands. We show these band structures for the fcc, bcc, and hexagonal lattice in Figs. 3.1, 3.2, and 3.3, respectively. Note, however, that we are

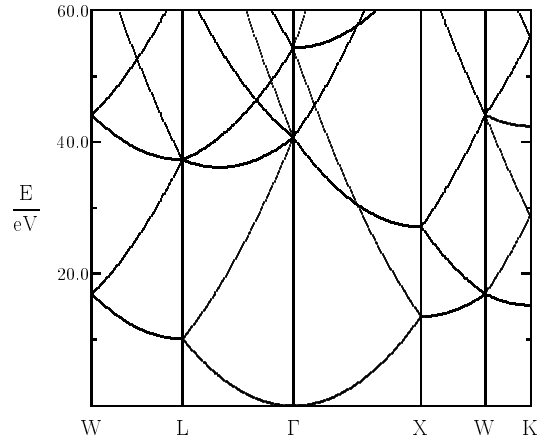


Figure 3.1: Free electron dispersion curves for the fcc lattice along selected symmetry lines of the first Brillouin zone. The points indicated are the same as in Fig. 2.18.

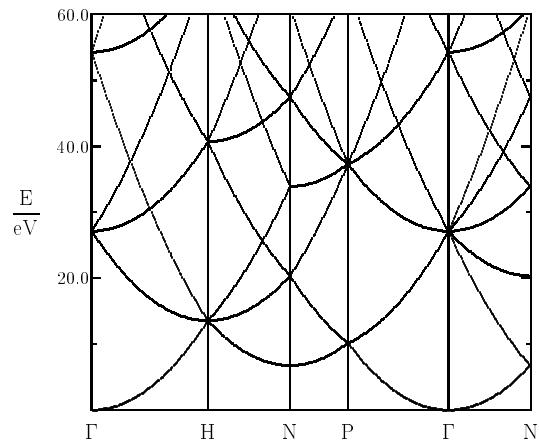


Figure 3.2: Free electron dispersion curves for the bcc lattice along selected symmetry lines of the first Brillouin zone. The points indicated are the same as in Fig. 2.19.

merely displaying intersecting parabolas along the high symmetry lines of the

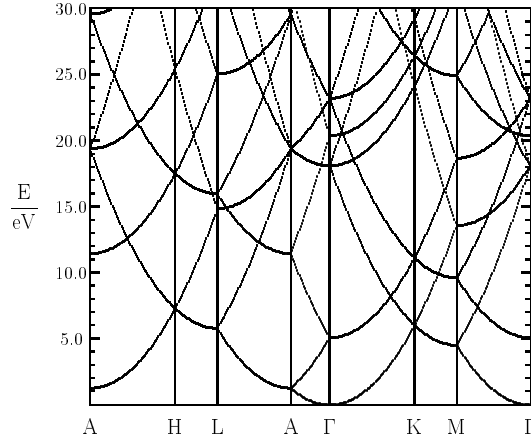


Figure 3.3: Free electron dispersion curves for the hexagonal lattice along selected symmetry lines of the first Brillouin zone. The points indicated are the same as in Fig. 2.20.

corresponding Brillouin zones.

Quantum mechanics is incorporated into the Sommerfeld theory via the Pauli exclusion principle, which we will discuss in detail in Sec. 5.2. It states that in a system of fermions each single particle level can be occupied by at most one particle. In the present case the single particle states are characterized by the \mathbf{k} vector and the electron spin $\sigma = \pm\frac{1}{2}$. We will thus successively fill the $N/2$ lowest lying electron levels $\varepsilon_{\mathbf{k}}$, each with two electrons. Due to the isotropic dispersion relation (3.1.4) the resulting volume in \mathbf{k} space will be a sphere for large electron numbers N with the radius of this sphere, which is called the Fermi wave vector k_F , being fixed by

$$\frac{4\pi k_F^3}{3} = \frac{N}{2} \Omega_{\mathbf{k}} = \frac{N(2\pi)^3}{2N_{UC}\Omega_{UC}} \quad . \quad (3.1.5)$$

Here we have used Eq. (2.6.7). Since the (uniform) (valence) electron density is given by

$$\rho = \frac{N}{N_{UC}\Omega_{UC}} \quad (3.1.6)$$

we obtain the relation

$$\rho = \frac{k_F^3}{3\pi^2} \quad . \quad (3.1.7)$$

Of course, the Fermi sphere allows to define several quantities analogous to the Fermi wave vector as there are

$$\begin{aligned} \text{the Fermi momentum} \quad p_F &= \hbar k_F \quad , \\ \text{the Fermi velocity} \quad v_F &= \frac{p_F}{m} \quad , \end{aligned}$$

$$\text{the Fermi energy } E_F = \frac{\hbar^2 k_F^2}{2m} ,$$

$$\text{and the Fermi temperature } T_F = \frac{E_F}{k_B} .$$

Finally, the surface of the sphere is called the Fermi surface.

Following common practice we express the density in terms of the density parameter r_S as

$$\frac{4\pi}{3} r_S^3 = \frac{1}{\rho} , \quad (3.1.8)$$

which is just the radius of a sphere containing one valence electron, and may then write the Fermi wave vector as

$$k_F = \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{1}{r_s} = \frac{1.92}{r_s} . \quad (3.1.9)$$

Using the Bohr radius

$$a_B = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.529 \cdot 10^{-10} \text{m} \quad (3.1.10)$$

we obtain for the Fermi energy

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{\frac{2}{3}} = \frac{1}{2} \frac{e^2 a_B}{4\pi\epsilon_0} k_F^2 = \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} \right) (k_F a_B)^2 , \quad (3.1.11)$$

where the first factor is the atomic energy unit,

$$1\text{Ryd} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} = 13.6058\text{eV} , \quad (3.1.12)$$

which is identical to the ground state binding energy of the hydrogen atom. Combining Eqs. (3.1.9) and (3.1.11) we get

$$E_F = \frac{(9\pi/4)^{\frac{2}{3}}}{(r_s/a_B)^2} \text{Ryd} = \frac{(1.92)^2}{(r_s/a_B)^2} \text{Ryd} = \frac{50.1}{(r_s/a_B)^2} \text{eV} . \quad (3.1.13)$$

For most metallic elements, r_s/a_B is between 2 and 3 and the Fermi energy thus lies in the range of 5 to 13 eV. It is interesting to evaluate from this the corresponding Fermi temperatures, which are of the order of 10^5 K, hence, much higher than room temperature. From this simple estimate it becomes clear that in most cases it is a well justified approximation to resort to the ground state ($T = 0$ K) in describing the electronic properties of most materials.

As mentioned in Sec. 2.7 the calculation of a lot of physical quantities requires knowledge of the density of states as defined by Eq. (2.7.6). Combining it with the isotropic dispersion relation (3.1.4) and taking into account the spin degeneracy of the electronic states we write

$$\begin{aligned} \rho(E) &= \frac{2}{\Omega_{BZ}} \sum_n \int_{\Omega_{BZ}} d^3\mathbf{k} \delta(E - \varepsilon_{n\mathbf{k}}) \\ &= \frac{8\pi}{\Omega_{BZ}} \int k^2 dk \delta(E - \varepsilon_{\mathbf{k}}) , \end{aligned} \quad (3.1.14)$$

where in the second line the integration extends over all reciprocal space. However, while in the first line the δ distribution accounts for all the parabolas centered at all lattice points \mathbf{K}_n of the reciprocal lattice, we consider only the single parabola centered at $\mathbf{k} = \mathbf{0}$ in the second integration. With the help of Eq. (3.1.4) as well as of the identity

$$d\varepsilon_{\mathbf{k}} = \frac{\hbar^2}{m} k dk \quad (3.1.15)$$

we then get the result

$$\begin{aligned} \rho(E) &= \frac{8\pi}{\Omega_{BZ}} \frac{m}{\hbar^2} \frac{\sqrt{2m}}{\hbar} \int d\varepsilon_{\mathbf{k}} \sqrt{\varepsilon_{\mathbf{k}}} \delta(E - \varepsilon_{\mathbf{k}}) \\ &= \frac{4\pi\Omega_{UC}}{(2\pi)^3} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{E} \\ &= \frac{\Omega_{UC}}{2\pi^2} k_F^3 \frac{1}{E_F^{\frac{3}{2}}} \sqrt{E} \\ &= \frac{3}{2} \Omega_{UC} \frac{\rho}{E_F} \sqrt{\frac{E}{E_F}} \quad . \end{aligned} \quad (3.1.16)$$

Here we have used Eqs. (2.6.7), (3.1.6), (3.1.7), and (3.1.11). Integrating the density of states to the Fermi energy we obtain

$$\begin{aligned} \int_{-\infty}^{E_F} dE \rho(E) &= \frac{3}{2} \Omega_{UC} \frac{\rho}{E_F} \int_0^{E_F} dE \sqrt{\frac{E}{E_F}} \\ &= \frac{3}{2} \Omega_{UC} \rho \int_0^1 dx \sqrt{x} \quad \text{where } x = \frac{E}{E_F} \quad , \quad dx = \frac{dE}{E_F} \\ &= \Omega_{UC} \rho \\ &= \frac{N}{N_{UC}} \quad , \end{aligned} \quad (3.1.17)$$

which is just the number of electrons per unit cell. In close analogy we evaluate the energy per electron as

$$\begin{aligned} \frac{E^{(0)}}{N} &= \frac{N_{UC}}{N} \int_{-\infty}^{E_F} dE E \rho(E) \\ &= \frac{3}{2} \int_0^{E_F} dE \left(\frac{E}{E_F}\right)^{\frac{3}{2}} \\ &= \frac{3}{2} E_F \int_0^1 dx' (x')^{\frac{3}{2}} \\ &= \frac{3}{2} E_F \frac{2}{5} \\ &= \frac{3}{5} E_F \quad . \end{aligned} \quad (3.1.18)$$

We complement this expression with that of the (constant) energy density,

$$\begin{aligned} \frac{1}{\Omega_{UC}} \int_{-\infty}^{E_F} dE E \rho(E) &= \frac{3}{5} \rho E_F \\ &= \frac{3}{5} \rho \frac{\hbar^2 k_F^2}{2m} \\ &= \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2)^{\frac{2}{3}} (\rho)^{\frac{5}{3}} \quad , \end{aligned} \quad (3.1.19)$$

which will be needed as the starting point of Thomas-Fermi theory. Finally combining Eqs. (3.1.18) and (3.1.13) we get

$$\frac{E^{(0)}}{N} = \frac{2.21}{(r_s/a_B)^2} \text{Ryd} \quad . \quad (3.1.20)$$

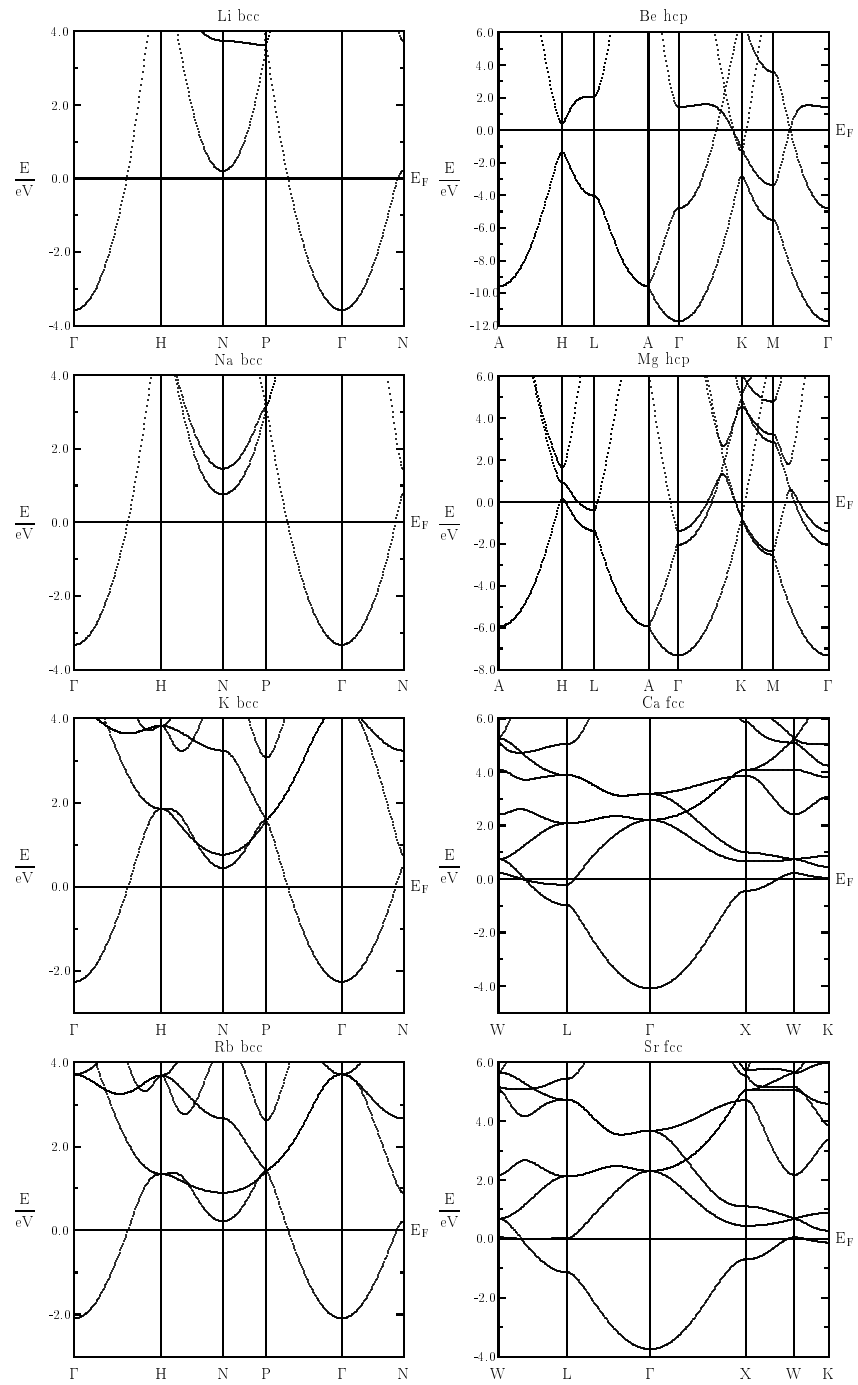
3.2 Simple Metals

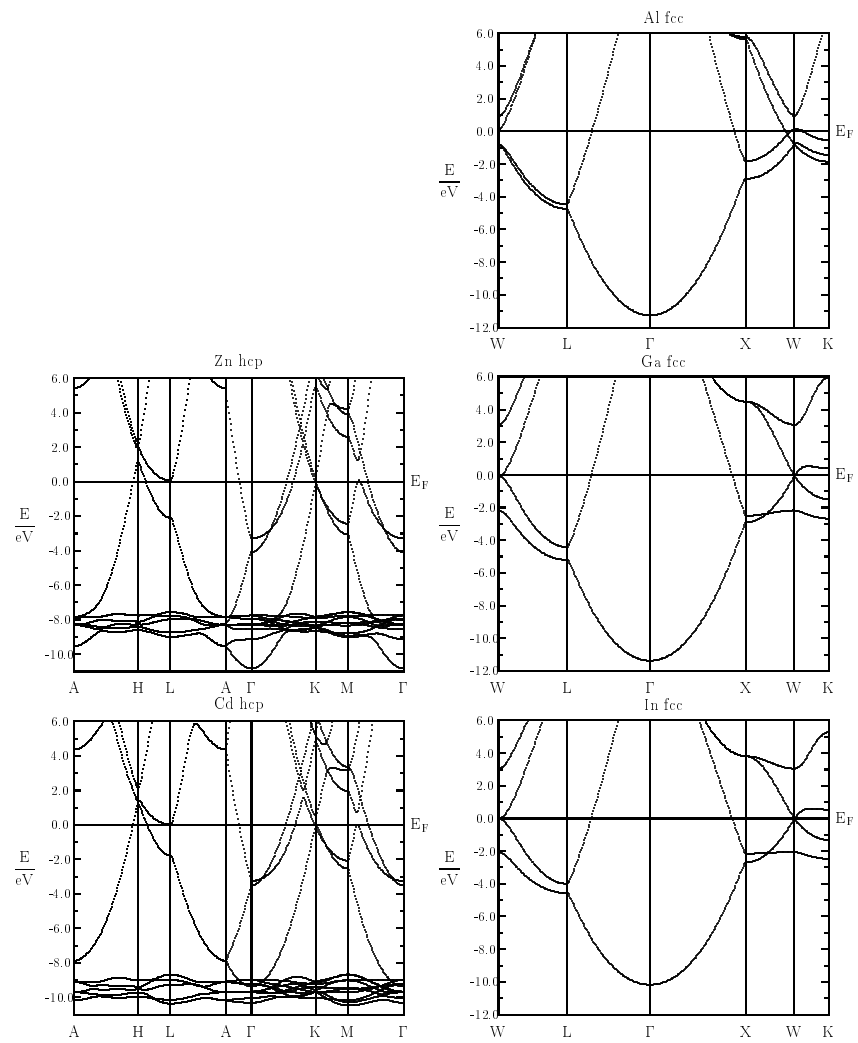
Of course, in view of the crude approximations underlying the Sommerfeld theory of metals we may ask how well it is able to describe the properties of real materials. Initially, the theory was invented by Sommerfeld in order to describe the electronic properties especially of the simple metals. For this reason we shall have a closer look at this class of elements. In the schematic periodic table given in Fig. 3.4 we have highlighted the *sp*-bonded metals to be

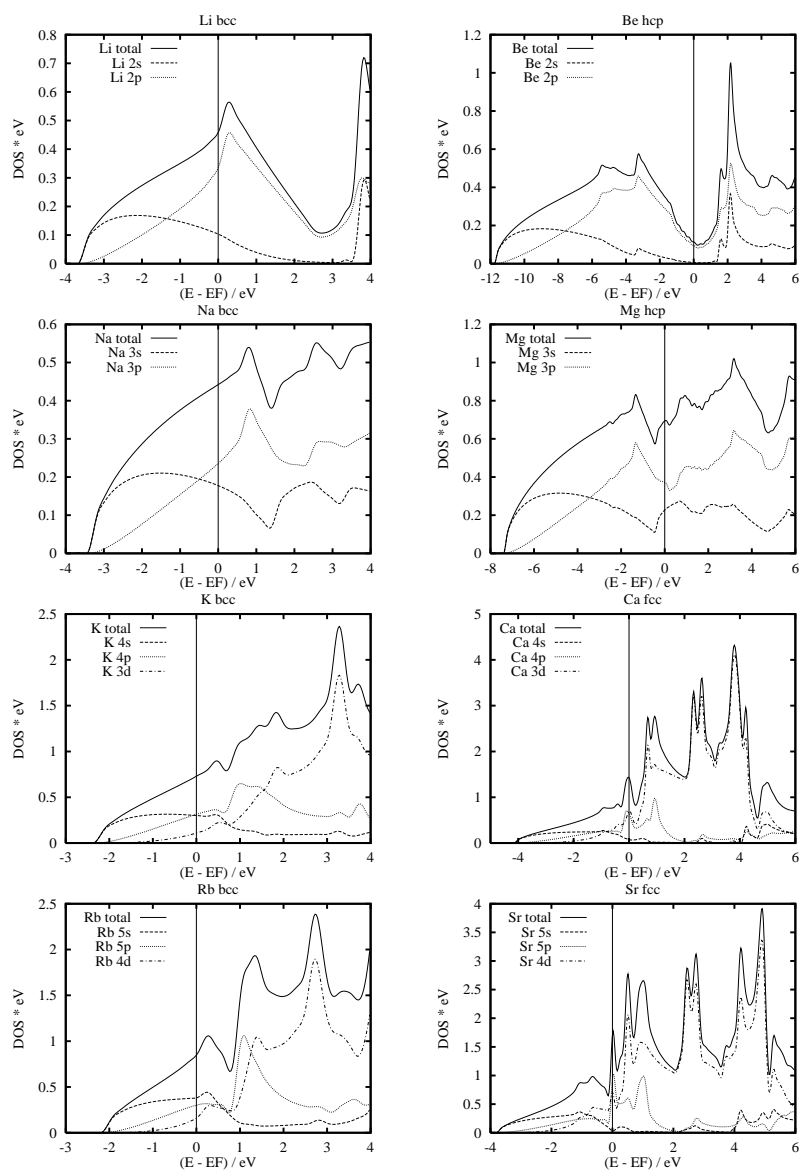
Li	Be				2p
Na	Mg			Al	3p
K	Ca	3d	Zn	Ga	4p
Rb	Sr	4d	Cd	In	5p

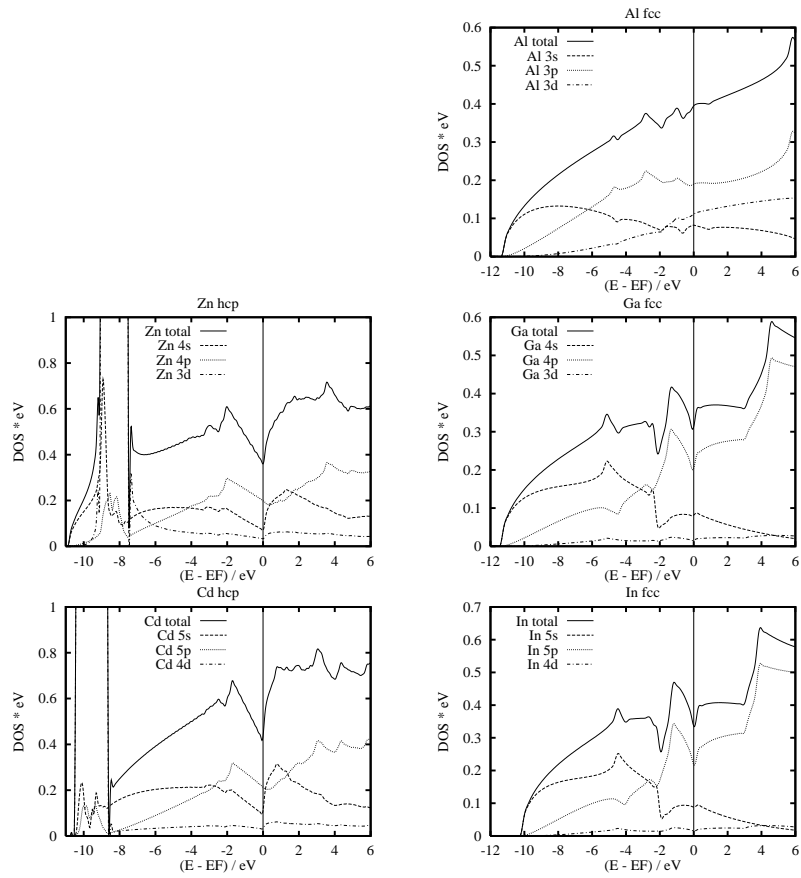
Figure 3.4: Section of the periodic table.

discussed in the present section. The band structures as well as the total and partial, i.e. the angular momentum projected densities of states (DOS) of these elements are displayed in Figs. 3.5, 3.6, 3.7, and 3.8. They grew out of self-consistent calculations as based on density functional theory within the local density approximation, which were performed using the augmented spherical wave (ASW) method [172, 48] in its relativistic implementation but ignoring spin-orbit coupling. Although the exact shape of the partial DOS depends on the particular decomposition of the total DOS they nevertheless give a good

Figure 3.5: Electronic bands of sp -valent metals.

Figure 3.6: Electronic bands of *sp*-valent metals.

Figure 3.7: Total and partial densities of states (DOS) of sp -valent metals.

Figure 3.8: Total and partial densities of states (DOS) of *sp*-valent metals.

measure for the energy dependent distribution of the electronic states among the orbitals involved.

In a first step the band structures and the DOS shown in Figs. 3.5, 3.6, 3.7, and 3.8 should be related to the free electron dispersion curves displayed in Figs. 3.1 to 3.3 as well as to the square root dependence of the free electron density of states, Eq. (3.1.16). Obviously, Na, Mg, and Al across the second period and Al, Ga, and In down group III are good nearly free electron (NFE) metals. In the 3rd and 4th period elements left to Ga and In the NFE behaviour, although still visible in the lower energy range, is distorted by the presence of the d -states. A different kind of distortion show the densities of states of the first period elements Li and Be. In general, due to the different number of valence electrons the DOS of the alkali metals are NFE-like up to the Fermi energy whereas the increased electron count of the group II elements leads to a distinct minimum at E_F in particular for the hexagonal metals. The latter effect becomes visible for Zn and Cd due to our scaling of the DOS curves, which ignores the high DOS of the filled d -states. Moreover, we point to the dominating influence of s -states at the bottom of the bands of all the sp -valent metals (except for Zn and Cd), which is superseded by a growing p -character as the energy increases.

Going into more detail we turn to aluminum, which band structure deviates only little from the free electron dispersion, Fig. 3.1. The major change is the band splitting along the symmetry lines W - L and X - W - K (Note, that the free electron bands have been calculated for a different lattice constant and hence show a different scaling). The nearly free electron behaviour of this metal has been confirmed by comparisons of deHaas-van Alphen data with free electron Fermi surface calculations the latter also explaining the positive sign of the Hall coefficient [10]. The full band structure has been determined via angle-resolved photoemission (ARUPS) experiments by Levinson *et al.* who compared their results to electronic structure calculations by Singhal and Callaway [100, 147]. Some of these results are depicted in Fig. 3.9, which reveal a generally good agreement. Yet, a distinct difference should be noted which consists of the deviations concerning the position of the highest occupied state at both Γ and X. Such differences occur in all the simple metals the most striking example probably being Na and have been the subject of intensive discussion until recently (see [46] for more details).

Having gained some experience from Al we now turn to the abovementioned deviations from NFE like electronic states visible for Li and Be. They are quite obvious from both the DOS and the band structure. Comparing, in particular, Be to Mg we observe the deeper minimum of the DOS at E_F . It can be traced back to the shifts of the highest occupied states at L, Γ , and M of the Mg bands, which are several eV higher in energy for Be. The resulting gaps amount to 6 and 2 eV, respectively, which is much larger than the 1 eV gap present at the X point of Al. The changes appearing when going from Mg to Be, however, are readily explained by the fact that the first row elements have no p -core electrons and hence the screening of the nuclear Coulomb potential is much reduced. This effect is less pronounced for the $2p$ - than for the $2s$ -electrons,

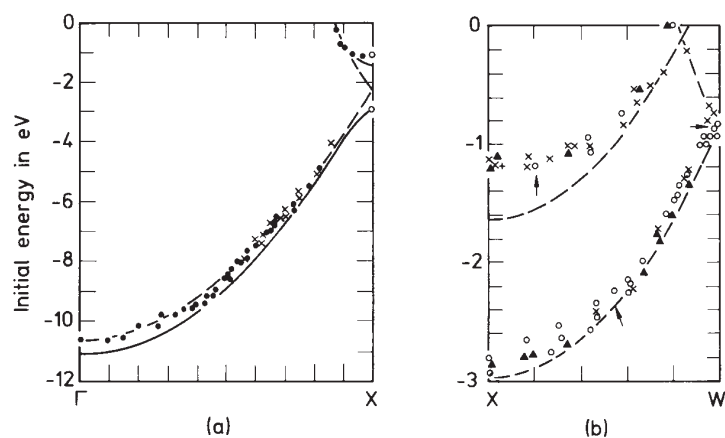


Figure 3.9: Experimental band structure of Al as obtained by Levinson et. al. from ARUPS [100], compared to calculations by Singhal and Callaway [147]. (a) Bands along $\Gamma - X$: free electron calculations with an effective mass $m^* = 1.1m$ (dashed) and electronic structure calculations by Singhal and Callaway (solid); (b) Bands along $X - W$: electronic structure calculations by Singhal and Callaway (dashed). Reproduced by permission of The American Physical Society from H. J. Levinson, F. Greuter, and E. W. Plummer, *Experimental band structure of aluminum*, Phys. Rev. B **27**, 727 (1983).

which are closer to the nucleus. Since of the three states mentioned before those at L and Γ contain a higher $2s$ contribution as compared to the corresponding state at the M point (note e.g. the relative $2s$ - and $2p$ -contributions to the DOS at -3.2 eV and 1.5 – 2.0 eV, respectively) the energetic shifts are larger for the former two points.

In closing this section we complement the band structures of the simple metals as shown in Figs. 3.5 and 3.6 by that of fcc Ni as given in Fig. 3.10. On comparing this band structure to that of fcc Al we observe rather good agreement in the low energy region up to approximately 2.5 eV below the Fermi energy. In particular, the parabolic behaviour is clearly visible. In contrast, there are substantial deviations from the free electron behaviour in the vicinity of the Fermi energy due to the appearance of five rather flat bands in the region $[-2.5 : 0]$ eV. These are the Ni $3d$ states, which are much more localized and, hence, display only a small dispersion. Yet, by hybridizing with the s and p parabolic bands they distort these bands considerably and only at energies above the E_F the parabolic behaviour of the latter is restored. To conclude, even in the transition metal series free electron behaviour is still present albeit with distortion in the energy region of the more localized d states. While this is generally true for all the transition metals, the position of the d level of course varies due to the increased occupation of these bands across the series.

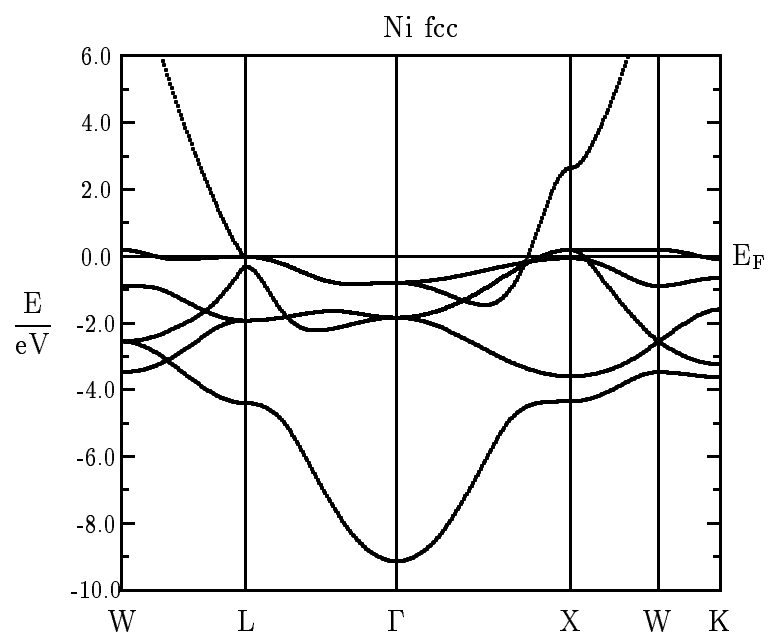


Figure 3.10: Electronic bands of Ni.

Chapter 4

The electronic ground state

4.1 Independent electron approximation

Having approximately separated the ionic and electronic degrees of freedom we concentrate from now on on the electronic Hamiltonian (2.2.12), i.e.

$$\begin{aligned} H_0 &= H_0(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= H_{ion-ion}(\{\mathbf{R}_\mu\}) + H_{el}(\{\mathbf{r}_i\}) + H_{ion-el}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \quad , \quad (4.1.1) \end{aligned}$$

where the ionic positions now enter as parameters rather than dynamic variables. Using Eqs. (2.1.2) to (2.1.4) we may rewrite this Hamiltonian as

$$H_0 = H_{el,kin}(\{\mathbf{r}_i\}) + H_{ext}(\{\mathbf{r}_i\}) + H_{el-el}(\{\mathbf{r}_i\}) \quad , \quad (4.1.2)$$

where

$$H_{el,kin}(\{\mathbf{r}_i\}) = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 \right] \quad , \quad (4.1.3)$$

$$H_{el-el}(\{\mathbf{r}_i\}) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad , \quad (4.1.4)$$

$$\begin{aligned} H_{ext}(\{\mathbf{r}_i\}) &= H_{ion-ion}(\{\mathbf{R}_\mu\}) + H_{ion-el}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= \frac{1}{2} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} V_{ion-ion}(\mathbf{R}_\mu - \mathbf{R}_\nu) + \sum_i \left[\sum_\mu V_{ion-el}(\mathbf{r}_i - \mathbf{R}_\mu) \right] \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z_{val,\mu} Z_{val,\nu}}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} - \frac{e^2}{4\pi\epsilon_0} \sum_i \sum_\mu \frac{Z_{val,\mu}}{|\mathbf{R}_\mu - \mathbf{r}_i|} \\ &=: \sum_i v_{ext}(\mathbf{r}_i) \quad . \quad (4.1.5) \end{aligned}$$

Here, we have combined the ion-ion and ion-electron interaction to the so-called external potential. Note that the term “external” does not indicate that the

ions are outside the solid but that the ions can be distinguished from the identical electrons as an entity of themselves. Eventually, we are in a position to write the Hamiltonian as

$$\begin{aligned} H_0 &= \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right] + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &=: H_0^{\{1\}} + H_0^{\{2\}} \quad , \end{aligned} \quad (4.1.6)$$

i.e. as the sum of a single particle term and an interaction term. While the former comprises a single sum over terms, which act in the same way onto all electrons, the last term, $H_0^{\{2\}}$, represents the electron-electron interaction and gives rise to an additional potential for each electron.

Since the Hamiltonian (4.1.6) involves all the electrons the wave function growing out of Schrödinger's equation (2.2.2)

$$\psi_{\bar{\alpha}} = \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \quad , \quad (4.1.7)$$

is a many-particle wave function, which likewise depends on all the electronic coordinates.

An idealized form of the Hamiltonian (4.1.6) results from the independent particle approximation already mentioned in Sec. 3.1, where the electron-electron interaction is completely neglected. In this case the Hamiltonian falls into a sum of single particle Hamiltonians

$$H_0 \approx H_0^{\{1\}} = \sum_i H_0^{(i)}(\mathbf{r}_i, \{\mathbf{R}_\mu\}) \quad , \quad (4.1.8)$$

where each

$$H_0^{(i)}(\mathbf{r}_i, \{\mathbf{R}_\mu\}) = -\frac{\hbar^2}{2m} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \quad , \quad (4.1.9)$$

acts on a single electron only. As a consequence, all these single particle Hamiltonians commute

$$\left[H_0^{(i)}, H_0^{(j)} \right] = 0 \quad , \quad (4.1.10)$$

and we are able to specify the complete wave function by first solving the much simpler single particle problems

$$H_0^{(i)} \chi_{\alpha_i}(\mathbf{r}_i, \{\mathbf{R}_\mu\}) = E_{\alpha_i} \chi_{\alpha_i}(\mathbf{r}_i, \{\mathbf{R}_\mu\}) \quad , \quad (4.1.11)$$

and then building the many-body wave functions as the direct product of the single particle eigenfunctions,

$$\psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) = \bigotimes_i \chi_{\alpha_i}(\mathbf{r}_i, \{\mathbf{R}_\mu\}) \quad \text{with } \bar{\alpha} = \{\alpha_i\} \quad . \quad (4.1.12)$$

In general, any wave function can then be represented by an expansion in these direct products as

$$\psi(\{\mathbf{r}_i, \mathbf{R}_\mu\}) = \sum_{\bar{\alpha}} c_{\bar{\alpha}} \psi_{\bar{\alpha}}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \quad . \quad (4.1.13)$$

Since each $H_0^{(i)}$ acts only on one of the factors, reproducing it with an prefactor E_{α_i} , these product wave functions obviously solve Schrödinger's equation (2.2.2) with the eigenvalues given by

$$E_{\bar{\alpha}} = \sum_i E_{\alpha_i} \quad . \quad (4.1.14)$$

Two points deserve special attention:

- Even in case that the Hamiltonian (4.1.6) can be expressed as the sum (4.1.8) of single particle Hamiltonians (4.1.9), Eq. (4.1.12) is valid only for distinguishable particles. In contrast, for identical particles the many-body wave function must obey additional symmetries, which are related to the exchange of particles. This will be the subject of the following chapter.
- If the electron-electron interaction cannot be neglected the wave function turns into a correlated function, which can no longer be written as a direct product. Nevertheless, since the product wave functions (4.1.12) of the uncorrelated problem form a complete set, they may still serve as basis functions in an expansion of the solution to the full problem like in Eq. (4.1.13). This goes under the term “configuration interaction”. A different approach arises from approximating the electron-electron interaction by an effective single-particle potential. In this case the complete wave function could still be written as a product of single particle wave functions with the external potential v_{ext} complemented by the so reduced pair potential. Hartree-Fock as well as density functional theory go along this line, which we will discuss in much more detail in later chapters. A simpler approach consists of the Hartree method, which ignores the previous remark, hence, the identity of the electrons. However, it still makes clear the main ideas and for this reason will be described in the present chapter. Thus our qualitative discussion of the independent particle approximation reaches far beyond the rather pedagogical aspects emphasized above.

Like Hartree-Fock as well as density functional theory the Hartree method aims especially at the electronic ground state. Note that concentrating on the ground state actually is not a restriction in view of the rather high Fermi temperatures discussed in Sec. 3.1. For the ground state the minimum property of the total energy suggests to employ a variational procedure for the approximate calculation of the electronic wave function. It is thus worthwhile to take a closer look at the underlying variational approach before we deal with the Hartree method.

4.2 The variational principle

The variational methods are based on the rather general variational principle, which identifies the extremal expectation values of a given operator with its

eigenvalues. In order to be concrete we consider the eigenvalue problem of an Hermitian operator A defined in Hilbert space \mathcal{H} and write down the following theorem:

Any state $|\psi\rangle$ within the Hilbert space \mathcal{H} , which has a finite norm and for which the expectation value

$$\langle A \rangle_\psi = \frac{\langle \psi | A | \psi \rangle}{\langle \psi | \psi \rangle} \quad (4.2.1)$$

of an Hermitian operator A is stationary, is an eigenvector of the discrete spectrum of A with eigenvalue $\langle A \rangle_\psi$, and conversely.

In order to prove this theorem we first note that the expectation value obviously is stationary when the variation vanishes, i.e.

$$\delta \langle A \rangle_\psi \stackrel{!}{=} 0 \quad . \quad (4.2.2)$$

Since

$$\begin{aligned} \delta \langle A \rangle_\psi &= \frac{1}{\langle \psi | \psi \rangle} \delta \langle \psi | A | \psi \rangle - \frac{1}{\langle \psi | \psi \rangle^2} \langle \psi | A | \psi \rangle \delta \langle \psi | \psi \rangle \\ &= \frac{1}{\langle \psi | \psi \rangle} \left[\delta \langle \psi | A | \psi \rangle - \langle A \rangle_\psi \delta \langle \psi | \psi \rangle \right] \\ &= \frac{1}{\langle \psi | \psi \rangle} \left[\langle \delta \psi | (A - \langle A \rangle_\psi \mathcal{I}) | \psi \rangle + \langle \psi | (A - \langle A \rangle_\psi \mathcal{I}) | \delta \psi \rangle \right] \quad , \end{aligned} \quad (4.2.3)$$

this condition is fulfilled if

$$\langle \delta \psi | (A - \langle A \rangle_\psi \mathcal{I}) | \psi \rangle + \langle \psi | (A - \langle A \rangle_\psi \mathcal{I}) | \delta \psi \rangle = 0 \quad . \quad (4.2.4)$$

Here we have used the positive definiteness of the norm of the wave function. Still, we may not yet conclude that both terms on the left hand side vanish for, being the variations of the $\langle \psi |$ and $|\psi\rangle$, $\langle \delta \psi |$ and $|\delta \psi\rangle$ are not independent of each other. However, Eq. (4.2.4) will hold for any variation of the wave function. Taking, in particular, $i|\psi\rangle$, we obtain

$$|\delta(i\psi)\rangle = i|\delta\psi\rangle \quad , \quad \langle \delta(i\psi) | = -i\langle \delta\psi | \quad (4.2.5)$$

and from this

$$-i\langle \delta\psi | (A - \langle A \rangle_\psi \mathcal{I}) | \psi \rangle + i\langle \psi | (A - \langle A \rangle_\psi \mathcal{I}) | \delta\psi \rangle = 0 \quad . \quad (4.2.6)$$

Multiplying Eq. (4.2.6) by i and adding and subtracting, respectively, the result to and from Eq. (4.2.4) we arrive indeed at two independent equations,

$$\langle \delta\psi | (A - \langle A \rangle_\psi \mathcal{I}) | \psi \rangle = 0 \quad (4.2.7)$$

$$\langle \psi | (A - \langle A \rangle_\psi \mathcal{I}) | \delta\psi \rangle = 0 \quad . \quad (4.2.8)$$

Again, this holds for any variation and we are able to note

$$(A - \langle A \rangle_\psi \mathcal{I}) |\psi\rangle = 0 \quad (4.2.9)$$

$$(A^\dagger - \langle A \rangle_\psi^* \mathcal{I}) |\psi\rangle = 0 \quad . \quad (4.2.10)$$

Since A is Hermitian and, hence, has real eigenvalues both equations are identical. As a consequence, each wave function satisfying Eq. (4.2.2) is an eigenstate of the operator A with eigenvalue $\langle A \rangle_\psi$.

Conversely, if $|\psi\rangle$ is an eigenvector of the operator A with eigenvalue $\langle A \rangle_\psi$,

$$A|\psi\rangle = \langle A \rangle_\psi |\psi\rangle \quad , \quad (4.2.11)$$

multiplication with $\langle \psi|$ leads to Eq. (4.2.1). In addition, for an Hermitian operator A Eq. (4.2.11) results via Eq. (4.2.3) in Eq. (4.2.2), and the theorem is proven.

Although the above theorem holds for any Hermitian operator its important application arises for A being the Hamiltonian of a quantum mechanical system. Denoting the ground state by the subscript 0 we obtain the following lemma:

For any wave vector $|\psi\rangle$ the expectation value of the Hamiltonian H is greater or equal than the energy E_0 of the ground state,

$$\langle H \rangle_\psi \geq E_0 \quad . \quad (4.2.12)$$

In order to prove this inequality we use the spectral representation of H in terms of its eigenvalues E_i and projection operators Π_i on the respective eigenspaces and write

$$\begin{aligned} \langle H \rangle_\psi - E_0 &= \frac{\langle \psi | (H - E_0) | \psi \rangle}{\langle \psi | \psi \rangle} \\ &= \sum_{i=0}^{\infty} (E_i - E_0) \frac{\langle \psi | \Pi_i | \psi \rangle}{\langle \psi | \psi \rangle} \quad . \end{aligned} \quad (4.2.13)$$

Of course, this can be readily extended to a continuous spectrum. Unless $|\psi\rangle$ is the (nondegenerate) ground state, the sum comprises only positive contributions and Eq. (4.2.12) is thus valid.

4.3 The Ritz variational method

A well known application of the variational principle arises in form of the Rayleigh-Ritz variational method. It seeks for solutions of Schrödinger's equation in a space \mathcal{H}' more restricted than the Hilbert space \mathcal{H} . Within this space the wave function depends on a set of trial functions $|\chi_i\rangle$ and variational parameters α_i ,

$$|\psi\rangle = f(\{|\chi_i\rangle\}, \{\alpha_i\}) \quad . \quad (4.3.1)$$

In practice, the trial functions and the function f must be simple enough to allow for an easy calculation of the energy functional,

$$\langle H \rangle_\psi = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \quad , \quad (4.3.2)$$

and, at the same time, must closely approximate the full Hilbert space \mathcal{H} . For this reason, the choice of trial functions has a decisive influence on the quality of the final approximate solution.

Combining Eqs. (4.3.1) and (4.3.2) we write the energy as a function of the variational parameters as

$$\langle H \rangle_\psi = g(\{\alpha_i\}) \quad (4.3.3)$$

and evaluate the parameters from the variational principle

$$\frac{\partial}{\partial \alpha_i} \langle H \rangle_\psi \stackrel{!}{=} 0 \quad \forall i \quad (4.3.4)$$

as $\alpha_i^{(0)}$. Once these extremal values are fixed we are in a position to calculate the optimal approximation to the ground state wave function

$$|\psi^{(0)}\rangle = f\left(\{|\chi_i\rangle\}, \{\alpha_i^{(0)}\}\right) \quad (4.3.5)$$

as well as to the energy

$$\langle H \rangle_{\psi^{(0)}} = g\left(\{\alpha_i^{(0)}\}\right) \quad . \quad (4.3.6)$$

In practice, this procedure leads to very good results. Obviously, the energy (4.3.6) is closer to the exact value the closer the approximate wave functions approach its exact counterpart. However, due to the stationary property, Eq. (4.2.2), the difference of the energies is infinitesimal of higher order than the difference of the wave functions. As a consequence, the method is especially suited for evaluating the ground state energy.

A particularly appealing and actually much used realization of the Ritz variational method arises if the wave function $|\psi\rangle$ can be represented as a linear combination of the trial functions,

$$|\psi\rangle = \sum_{i=1}^m \alpha_i |\chi_i\rangle \quad . \quad (4.3.7)$$

In this case the restricted Hilbert space \mathcal{H}' likewise is a linear vector space and, hence, a subspace of the original Hilbert space \mathcal{H} .

Writing Eq. (4.3.4) in analogy to the second line of Eq. (4.2.3) as

$$\frac{\partial}{\partial \alpha_i} \langle H \rangle_\psi = \frac{1}{\langle \psi | \psi \rangle} \left[\frac{\partial}{\partial \alpha_i} \langle \psi | H | \psi \rangle - \langle H \rangle_\psi \frac{\partial}{\partial \alpha_i} \langle \psi | \psi \rangle \right] \stackrel{!}{=} 0 \quad (4.3.8)$$

and inserting into this Eq. (4.3.7), while remembering the positive definiteness of the norm, we obtain

$$\frac{\partial}{\partial \alpha_i} \sum_{kl} \alpha_k^* \alpha_l \left[\langle \chi_k | H | \chi_l \rangle - \langle H \rangle_\psi \langle \chi_k | \chi_l \rangle \right] \stackrel{!}{=} 0 \quad , \quad (4.3.9)$$

and from this the linear equation system

$$\sum_k \alpha_k^* \left[\langle \chi_k | H | \chi_i \rangle - \langle H \rangle_\psi \langle \chi_k | \chi_i \rangle \right] \stackrel{!}{=} 0 \quad , \quad (4.3.10)$$

which requires that the determinant of the coefficient matrix, the secular determinant, vanishes,

$$\left| \langle \chi_k | H | \chi_i \rangle - \langle H \rangle_\psi \langle \chi_k | \chi_i \rangle \right| \stackrel{!}{=} 0 \quad . \quad (4.3.11)$$

From this the approximate eigenvalues $\langle H \rangle_\psi^{(0)}$ as well as the corresponding eigenvectors

$$|\psi^{(0)}\rangle = \sum_{i=1}^m \alpha_i^{(0)} |\chi_i\rangle \quad (4.3.12)$$

can be accessed. In passing we note that in case of complex parameters α_i both the real and imaginary part of these parameters must be varied or, equivalently, both α_i and α_i^* .

4.4 The Hartree equations

A yet different realization of the Ritz variational method arises from applying it to the Hamiltonian (4.1.6) describing the system of ions and electrons and minimizing the energy functional with respect to the shape of the single-particle wave functions. This step, first taken by Hartree [72], will allow to go beyond the independent electron approximation (4.1.8) and to approximately include the electron-electron interaction covered by the last term of Eq. (4.1.6).

Although this latter contribution hinders representing the many-body wave function as a direct product of single-particle functions like in Eq. (4.1.12), we may nevertheless use this form as the starting point for the variational method. We thus write

$$\psi(\{\mathbf{r}_i, \mathbf{R}_\mu\}) = \bigotimes_i \chi_i(\mathbf{r}_i, \{\mathbf{R}_\mu\}) \quad , \quad (4.4.1)$$

where the single-particle functions are assumed to be normalized,

$$\int d^3\mathbf{r}_i \chi_i^*(\mathbf{r}_i, \{\mathbf{R}_\mu\}) \chi_i(\mathbf{r}_i, \{\mathbf{R}_\mu\}) = 1 \quad \forall i \quad . \quad (4.4.2)$$

Combining the approach (4.4.1) with the Hamiltonian (4.1.6) we calculate the energy functional as

$$\langle H_0 \rangle_\psi = \int d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \psi^* H_0 \psi$$

$$\begin{aligned}
&= \sum_i \int d^3\mathbf{r}_i \chi_i^*(\mathbf{r}_i) \left[-\frac{\hbar^2}{2m} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right] \chi_i(\mathbf{r}_i) \\
&\quad + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \int d^3\mathbf{r}_i \int d^3\mathbf{r}_j \chi_i^*(\mathbf{r}_i) \chi_j^*(\mathbf{r}_j) \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \chi_j(\mathbf{r}_j) \chi_i(\mathbf{r}_i) \quad ,
\end{aligned} \tag{4.4.3}$$

where we have suppressed the dependence of the single-particle functions on the (fixed) positions of the ions for simplicity in writing. In addition, we have used the normalization (4.4.2). In order to find the optimal single-particle functions we vary the expression (4.4.3) with respect to the $\chi_i^*(\mathbf{r}_i)$ and look for the zero's of the first variation. As already mentioned at the end of the previous section this includes variation of both $\chi_i^*(\mathbf{r}_i)$ and $\chi_i(\mathbf{r}_i)$, which, however, are not independent. As a consequence, if we want to treat $\chi_i^*(\mathbf{r}_i)$ and $\chi_i(\mathbf{r}_i)$ as independent functions, we have to include the normalization conditions (4.4.2) via Lagrange parameters and obtain the variational expression

$$\delta \left(\langle H_0 \rangle_\psi - \sum_{i=1}^N \lambda_i \int d^3\mathbf{r}_i \chi_i^*(\mathbf{r}_i) \chi_i(\mathbf{r}_i) \right) \stackrel{!}{=} 0 \quad . \tag{4.4.4}$$

Inserting into this Eq. (4.4.3) we arrive at

$$\begin{aligned}
&\sum_i \int d^3\mathbf{r}_i \delta\chi_i^*(\mathbf{r}_i) \left[-\frac{\hbar^2}{2m} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right. \\
&\quad \left. + \frac{1}{4\pi\epsilon_0} \sum_{\substack{j \\ j \neq i}} \int d^3\mathbf{r}_j \chi_j^*(\mathbf{r}_j) \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \chi_j(\mathbf{r}_j) - \lambda_i \right] \chi_i(\mathbf{r}_i) \stackrel{!}{=} 0 \quad .
\end{aligned} \tag{4.4.5}$$

The factor $\frac{1}{2}$ in the last term has vanished since $\chi_i^*(\mathbf{r}_i)$ appears twice in the double sum. Eq. (4.4.5) holds for arbitrary variations of the single-particle wave functions. Furthermore, it must be valid for any dependence of the single-particle functions on \mathbf{r}_i . As a consequence, the square bracket term in the integral entering Eq. (4.4.5) must vanish this leading to the Hartree equations

$$\begin{aligned}
&\left[-\frac{\hbar^2}{2m} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right. \\
&\quad \left. + \frac{1}{4\pi\epsilon_0} \sum_{\substack{j \\ j \neq i}} \int d^3\mathbf{r}_j \chi_j^*(\mathbf{r}_j) \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \chi_j(\mathbf{r}_j) - \lambda_i \right] \chi_i(\mathbf{r}_i) = 0 \quad ,
\end{aligned} \tag{4.4.6}$$

which have the character of single-particle equations, where the Lagrange parameters λ_i and the functions $\chi_i(\mathbf{r}_i)$ are the eigenvalues and eigenfunctions, respectively. In order to make this explicit we write the Hartree equations as

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + v_{eff}^{(i)}(\mathbf{r}_i) \right] \chi_i(\mathbf{r}_i) = \lambda_i \chi_i(\mathbf{r}_i) \quad , \tag{4.4.7}$$

with the effective single-particle potential

$$v_{eff}^{(i)}(\mathbf{r}_i) = v_{ext}(\mathbf{r}_i) + \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{j \\ j \neq i}} \int d^3\mathbf{r}_j \frac{|\chi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} . \quad (4.4.8)$$

While the first two contributions, the kinetic energy and the external potential produced by the ions, are already known from the independent particle approximation, Eqs. (4.1.8) and (4.1.9), the last term in Eq. (4.4.8) is new. This so-called Hartree potential represents a repulsive potential arising from the interaction with the remaining $N - 1$ electrons. However, note that only the integral over all other single-particle wave functions enters and, hence, their particular form is washed out. For this reason, this approach of including only the Coulomb potential arising from an average charge distribution of the remaining electrons has proven very useful for metallic systems but we might need more refined approximations to the electronic problem once the spatial structure of their wave functions becomes more pronounced.

As is obvious from Eq. (4.4.8), the Hartree potential contains the square of the single-particle wave functions and, hence, strictly speaking, can be evaluated only *after* the single-particle wave functions have been determined via Eq. (4.4.7), which, however, itself depends on the effective potential. The dilemma is resolved by starting from a first guess for the effective potential, inserting this into Eq. (4.4.7) and evaluating a first approximation to the single-particle wave functions $\chi_i(\mathbf{r}_i)$. Once this has been done an improved version of the effective potential can be calculated via Eq. (4.4.8), which again enters Eq. (4.4.7). This establishes a cycle of successive evaluations of these two equations, which have to be iterated until the required accuracy is attained. The wave functions is thus determined *self-consistently* and for this reason the procedure is called the *self-consistent field* method.

As already mentioned at the end of Sec. 4.1 the simple product ansatz (4.1.12)/(4.4.1) does not reflect the fact that the electrons in a solid are identical, hence, cannot be distinguished. As a consequence, the Hartree equations do not provide a correct prescription of a system of identical particles. This is signalled by the fact that in the effective potential as given by Eq. (4.4.8) the double sum excludes the term $i = j$ and thus still depends on the particular electron it is applied to. In other words, the Hartree potential still allows to distinguish the electrons in a many-body system. In the following chapter we will learn about means to account for the identity of the electrons, which lay ground for the more refined Hartree-Fock as well as density functional theories. Nevertheless, the main route for evaluating the electronic states, i.e. the variational procedure and the self-consistent field method, will stay the same and thus its previous outline has a more general character.

Chapter 5

The electronic many-body problem

5.1 Identical particles

For a quantum mechanical systems of identical particles the construction of the Hilbert space as a product of single particle spaces with wave functions arising as simple direct products

$$|\chi_{\bar{\alpha}}\rangle = \bigotimes_i^N |\chi_{\alpha_i}^{(i)}\rangle \quad \text{with } \bar{\alpha} = \{\alpha_i\} \quad , \quad (5.1.1)$$

needs some modifications. Here we have omitted the spatial coordinates of the particles; α_i labels the single particle states of particle i and the upper index labels the individual particles.

In classical mechanics the identity of particles does not have substantial consequences, since each particle passes through a well defined trajectory and at the same time can be marked and identified without disturbing the system considerably. This is completely different in a quantum mechanical system, where marking a single particle corresponds to a measurement process and causes a substantial distortion of the particular state. We are thus faced with the fundamental quantum mechanical principle saying that identical particles can not be distinguished by any means.

Of course, this has drastic consequences for the form of the Hilbert space, the many-body wave function as well as the choice of operators. Besides being self-adjoint, operators for many-body systems must be fully symmetric with respect to all particles. Since, if any operator would allow to distinguish the particles they would no longer be identical. Needless to mention that each operator thus has to depend on all single particle variables in the same way.

Note that the just formulated requirement is, in particular, not fulfilled by the effective potential (4.4.8), hence, the effective Hamiltonian of the Hartree method where each particle experiences the potential generated by all *other*

particles. Since it is, in principle, fully correct to exclude the interaction of a particle with itself, the just mentioned deficiency of the Hartree potential (4.4.8) points to a defect in the assumptions underlying the derivation of the effective equations (4.4.7). While we will learn methods to overcome such defects in the present chapter, their application will give rise to an improved description of the electronic structure within Hartree-Fock theory, which we will turn to in Chap. 6.

For the wave functions the identity of all particles means that any permutation of particles must not change any expectation value. While becoming a bit more formal we nevertheless start out from the direct products (5.1.1) and define for each permutation

$$P : (1, 2, 3, \dots, N) \longrightarrow (P(1), P(2), P(3), \dots, P(N)) \quad (5.1.2)$$

of numbers $1, \dots, N$ a permutation operator by

$$\mathcal{P}_P \bigotimes_i^N |\chi_{\alpha_i}^{(i)}\rangle = \bigotimes_i^N |\chi_{\alpha_i}^{(P(i))}\rangle \quad , \quad (5.1.3)$$

which we have selected to permute the particles in the single particle states. Of course, we could have likewise opted for permuting the states while keeping the particles fixed. We are now able to formulate the above principle as

$$\begin{aligned} \langle \chi_{\bar{\alpha}} | \mathcal{P}_P^+ \mathcal{A} \mathcal{P}_P | \chi_{\bar{\alpha}} \rangle &= \bigotimes_i^N \bigotimes_j^N \langle \chi_{\alpha_i}^{(i)} | \mathcal{P}_P^+ \mathcal{A} \mathcal{P}_P | \chi_{\alpha_j}^{(j)} \rangle \\ &\stackrel{!}{=} \bigotimes_i^N \bigotimes_j^N \langle \chi_{\alpha_i}^{(i)} | \mathcal{A} | \chi_{\alpha_j}^{(j)} \rangle = \langle \chi_{\bar{\alpha}} | \mathcal{A} | \chi_{\bar{\alpha}} \rangle \quad , \quad (5.1.4) \end{aligned}$$

valid for any operator \mathcal{A} .

For N particles there exist $N!$ such permutations, which form a non-Abelian group, the *symmetric group* S_N . As well known, all permutations can be represented as products of the transpositions T_{ij} , which merely exchange two particles and thus may be regarded as fundamental permutations. For N particles, there exist $\frac{1}{2}N(N-1)$ such transpositions. Applying a transposition operator $\mathcal{T}_{ij} = \mathcal{P}_{T_{ij}}$ twice we obtain

$$\mathcal{T}_{ij}^2 = \mathcal{I} \quad \Longleftrightarrow \quad \mathcal{T}_{ij} = \mathcal{T}_{ij}^{-1} \quad , \quad (5.1.5)$$

where \mathcal{I} is the unity operator. The non-Abelian property of S_N derives from the fact that already the \mathcal{T}_{ij} in general do not commute,

$$[\mathcal{T}_{ij}, \mathcal{T}_{kl}] \neq 0 \quad , \quad (5.1.6)$$

unless they have no elements in common. Although the representation of a specific permutation by transpositions itself is not unique, each permutation

comprises either even or odd transpositions. The parity of the permutation, i.e. the quantity

$$(-)^P = (-1)^{\text{Number of transpositions making } P} \quad (5.1.7)$$

is thus fixed. This allows to distinguish even $((-)^P = +1)$ and odd $((-)^P = -1)$ elements of the group S_N .

Since Eq. (5.1.4) holds for any N -particle state it is also valid for arbitrary matrix elements, which may be written as

$$\begin{aligned} & \langle \chi | \mathcal{A} | \psi \rangle \\ &= \frac{1}{4} \left\{ \langle \chi + \psi | \mathcal{A} | \chi + \psi \rangle - \langle \chi - \psi | \mathcal{A} | \chi - \psi \rangle \right. \\ & \quad \left. + i \langle \chi - i\psi | \mathcal{A} | \chi - i\psi \rangle - i \langle \chi + i\psi | \mathcal{A} | \chi + i\psi \rangle \right\} , \quad (5.1.8) \end{aligned}$$

and, hence, for the operators themselves,

$$\mathcal{P}_P^+ \mathcal{A} \mathcal{P}_P = \mathcal{A} \quad . \quad (5.1.9)$$

In particular, for $\mathcal{A} = \mathcal{I}$ we have

$$\mathcal{P}_P^+ \mathcal{P}_P = \mathcal{I} \quad . \quad (5.1.10)$$

The permutation operators are thus unitary operators

$$\mathcal{P}_P^+ = \mathcal{P}_P^{-1} \quad , \quad (5.1.11)$$

and, multiplying Eq. (5.1.9) from the left with \mathcal{P}_P , we arrive at the important result

$$\mathcal{A} \mathcal{P}_P = \mathcal{P}_P \mathcal{A} \quad , \quad (5.1.12)$$

hence,

$$\boxed{[\mathcal{P}_P, \mathcal{A}] \equiv 0 \quad \forall P \in S_N} \quad . \quad (5.1.13)$$

For the description of a system of identical particles only those operators come into question, which commute with all permutations of the symmetric group S_N . This is the quantum mechanical formulation of the principle that identical particles cannot be distinguished.

As a consequence of Eq. (5.1.13), the possible many-body states must be simultaneous eigenstates of both the operators \mathcal{A} and all the permutation operators \mathcal{P}_P , hence, in particular, of all transposition operators \mathcal{T}_{ij} . While, due to Eq. (5.1.6), \mathcal{P}_P in general is not self-adjoint, the \mathcal{T}_{ij} are both self-adjoint and unitary operators according to Eqs. (5.1.5) and (5.1.11) and thus have eigenvalues ± 1 . This allows to distinguish two different types of many-body wave functions by their symmetry with respect to transpositions, namely

$$\text{symmetric functions:} \quad \mathcal{T}_{ij} |\psi\rangle = +|\psi\rangle \quad \forall i, j \quad (5.1.14)$$

$$\text{and antisymmetric functions:} \quad \mathcal{T}_{ij} |\psi\rangle = -|\psi\rangle \quad \forall i, j \quad .(5.1.15)$$

For this reason, of the $N!$ states (5.1.3) only two states come into question while the remaining $N! - 2$ states (for $N > 2$) violate Eq. (5.1.13) and, hence, must be ruled out. We thus note

The possible states of a system of identical particles are either symmetric or antisymmetric with respect to exchange of two particles!

As yet, it is not at all obvious that simultaneous eigenfunctions of all the transposition operators exist since in general they do not commute. However, we may construct such functions by means of the symmetrization and antisymmetrization operator

$$\mathcal{S} := \frac{1}{N!} \sum_{P \in S_N} \mathcal{P}_P \quad , \quad (5.1.16)$$

$$\mathcal{A} := \frac{1}{N!} \sum_{P \in S_N} (-)^P \mathcal{P}_P \quad , \quad (5.1.17)$$

which fulfil the identities

$$\mathcal{T}_{ij} \mathcal{S} = \sum_{P \in S_N} \mathcal{T}_{ij} \mathcal{P}_P = \sum_{P \in S_N} \mathcal{P}_P = +\mathcal{S} \quad (5.1.18)$$

$$\begin{aligned} \mathcal{T}_{ij} \mathcal{A} &= \sum_{P \in S_N} (-)^P \mathcal{T}_{ij} \mathcal{P}_P = - \sum_{P \in S_N} (-)^{T_{ij}P} \mathcal{T}_{ij} \mathcal{P}_P \\ &= - \sum_{P \in S_N} (-)^P \mathcal{P}_P = -\mathcal{A} \quad . \end{aligned} \quad (5.1.19)$$

We may thus construct symmetric and antisymmetric wave functions from the direct product (5.1.1) as

$$|\psi_+\rangle = \mathcal{S}|\chi_{\bar{\alpha}}\rangle = \mathcal{S} \bigotimes_i^N |\chi_{\alpha_i}^{(i)}\rangle \quad (5.1.20)$$

$$|\psi_-\rangle = \mathcal{A}|\chi_{\bar{\alpha}}\rangle = \mathcal{A} \bigotimes_i^N |\chi_{\alpha_i}^{(i)}\rangle \quad , \quad (5.1.21)$$

which indeed, according to Eqs. (5.1.18) and (5.1.19), fulfil Eqs. (5.1.14) and (5.1.15) as well as

$$\mathcal{P}_P |\psi_+\rangle = |\psi_+\rangle \quad \forall P \in S_N \quad , \quad (5.1.22)$$

$$\mathcal{P}_P |\psi_-\rangle = (-)^P |\psi_-\rangle \quad \forall P \in S_N \quad . \quad (5.1.23)$$

To summarize, since $|\psi_+\rangle$ and $|\psi_-\rangle$ are simultaneous eigenfunctions of all transposition operators with different eigenvalues $+1$ and -1 , respectively, they span one-dimensional orthogonal subspaces. Just to make this explicit we note

$$\langle \psi_- | \psi_+ \rangle = \langle \psi_- | \mathcal{T}_{ij} | \psi_+ \rangle = \langle \psi_- | \mathcal{T}_{ij}^+ | \psi_+ \rangle = -\langle \psi_- | \psi_+ \rangle \stackrel{!}{=} 0 \quad . \quad (5.1.24)$$

Since the permutation operators commute with the Hamiltonian the symmetry character of a many-body wave function is preserved for all times. Moreover, due to Eq. (5.1.13) there exists no measurement or preparation process at all to transfer a state from one subspace to the other, i.e. to change the symmetry character of the wave function. In passing we note that according to Eqs. (5.1.22) and (5.1.23) the permutation operators are self-adjoint operators within these two one-dimensional subspaces.

Within the $N!$ -dimensional space spanned by the states (5.1.3) for all permutations $P \in S_N$ the symmetric and antisymmetric states $|\psi_+\rangle$ and $|\psi_-\rangle$ thus define the only one-dimensional representation spaces of the group S_N . The remaining $N! - 2$ states (for $N > 2$) are of “mixed” symmetry; for each of these states exist two different transposition operators with different eigenvalues. As already mentioned above, these states thus do not fulfil Eqs. (5.1.14) and (5.1.15), hence, they do not obey the general physical principle (5.1.13) and can be omitted from further considerations.

So far, all our considerations were for a particular set of single particle states $|\chi_{\alpha_i}^{(i)}\rangle$, where each particle i occupied the state labelled α_i . For all the different single particle states α_i the states $|\psi_+\rangle$ and $|\psi_-\rangle$ span the fully symmetric Hilbert space $\mathcal{H}_N^{(+)}$ and the fully antisymmetric Hilbert space $\mathcal{H}_N^{(-)}$, respectively, while the states of mixed symmetry give rise to the higher dimensional Hilbert space $\mathcal{H}_N^{(M)}$. As a result, the complete Hilbert space falls into three orthogonal Hilbert subspaces,

$$\mathcal{H}_N = \mathcal{H}_N^{(+)} \oplus \mathcal{H}_N^{(-)} \oplus \mathcal{H}_N^{(M)} \quad , \quad (5.1.25)$$

and the operators (5.1.16) and (5.1.17) act as projection operators onto the physical Hilbert spaces. As an example we note for the antisymmetrization operator

$$\begin{aligned} \mathcal{A}^2 &= \frac{1}{(N!)^2} \sum_P \sum_{P'} (-)^P (-)^{P'} \mathcal{P}_P \mathcal{P}_{P'} = \frac{1}{(N!)^2} \sum_P \sum_{P'} (-)^{PP'} \mathcal{P}_{PP'} \\ &= \frac{1}{(N!)^2} \sum_{P'} \left\{ \sum_P (-)^P \mathcal{P}_P \right\} = \frac{1}{(N!)} \left\{ \sum_P (-)^P \mathcal{P}_P \right\} = \mathcal{A} \quad . \end{aligned} \quad (5.1.26)$$

5.2 Bosons and Fermions; Pauli principle

As seen in the previous section, the requirement of permutation symmetry of the possible many-body states led us to divide the complete Hilbert space into three orthogonal subspaces as noted in Eq. (5.1.25). According to Eq. (5.1.13) no state can change from one of these subspaces to another, neither by simple time evolution nor by any preparation process. Finally, states falling into the Hilbert space $\mathcal{H}_N^{(M)}$ were shown to violate Eq. (5.1.13) and we are thus left with the Hilbert spaces $\mathcal{H}_N^{(+)}$ and $\mathcal{H}_N^{(-)}$ of the fully symmetric and antisymmetric states.

Still, the question remains, which real systems can be assigned to these two Hilbert spaces. While a formal answer to this question can only be given within relativistic quantum field theory, experience shows that the so-called “spin-statistics theorem” [125] holds:

The Hilbert space of a system of identical particles with integer spin ($S = 0, 1, 2, \dots$) is the totally symmetric space $\mathcal{H}_N^{(+)}$ and the Hilbert space of a system of identical particles with half-integer spin ($S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$) is the totally antisymmetric space $\mathcal{H}_N^{(-)}$.

In quantum statistics the symmetry character of the many-body wave function of identical particles with integer and half-integer spin, respectively, causes them to obey either Bose-Einstein or Fermi-Dirac statistics and for this reason these particles are called bosons and fermions.

The many-body state of a system of bosons thus derives from Eq. (5.1.20) as

$$|\psi_+\rangle = C_+ \sum_{P \in S_N} \mathcal{P}_P \bigotimes_i^N |\chi_{\alpha_i}^{(i)}\rangle, \quad (5.2.1)$$

where we have left the normalization constant as yet unspecified. In particular, for two particles we write

$$|\psi_+\rangle = \begin{cases} \frac{1}{\sqrt{2}} \left[|\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle + |\chi_{\alpha_1}^{(2)}\rangle \otimes |\chi_{\alpha_2}^{(1)}\rangle \right] & \text{for } \alpha_1 \neq \alpha_2 \\ |\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle & \text{for } \alpha_1 = \alpha_2 \end{cases} \quad (5.2.2)$$

In contrast, for fermions we obtain from Eq. (5.1.21) for the totally antisymmetric state

$$|\psi_-\rangle = C_- \sum_{P \in S_N} (-)^P \mathcal{P}_P \bigotimes_i^N |\chi_{\alpha_i}^{(i)}\rangle, \quad (5.2.3)$$

which is formally identical to a determinant, the so-called Slater determinant,

$$|\psi_-\rangle = C_- \cdot \begin{vmatrix} |\chi_{\alpha_1}^{(1)}\rangle & |\chi_{\alpha_1}^{(2)}\rangle & \cdots & |\chi_{\alpha_1}^{(N)}\rangle \\ |\chi_{\alpha_2}^{(1)}\rangle & |\chi_{\alpha_2}^{(2)}\rangle & \cdots & |\chi_{\alpha_2}^{(N)}\rangle \\ \vdots & \vdots & & \vdots \\ |\chi_{\alpha_N}^{(1)}\rangle & |\chi_{\alpha_N}^{(2)}\rangle & \cdots & |\chi_{\alpha_N}^{(N)}\rangle \end{vmatrix}. \quad (5.2.4)$$

Again we have left the prefactor unspecified. Note that the products entering the Slater determinant according to Eq. (5.2.3) are direct products. In particular, for two particles Eq. (5.2.4) becomes

$$|\psi_-\rangle = \frac{1}{\sqrt{2}} \left[|\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle - |\chi_{\alpha_1}^{(2)}\rangle \otimes |\chi_{\alpha_2}^{(1)}\rangle \right]. \quad (5.2.5)$$

As is obvious from Eqs. (5.2.3) to (5.2.5) the antisymmetry with respect to particle exchange thus has the important consequence, that these states vanish

whenever two or more particles stay in the same single particle state. This observation leads to the Pauli principle:

In a system of identical fermions each single particle state can be occupied by at most one particle. In particular, two particles with the same spin can not stay at the same position and two particles at the same position must have opposite spin.

Again the independent particle approximation (4.1.8) gives a first qualitative insight into the nature of the many-body state. Within this approximation the many-body wave function fulfils Schrödinger's equation

$$H_0|\psi_{\pm}\rangle = E_{\bar{\alpha}}|\psi_{\pm}\rangle \quad (5.2.6)$$

with the energy $E_{\bar{\alpha}}$ given by Eq. (4.1.14). In order to prove this for the particular case $N = 2$ (with the two bosons occupying different states) we use Eq. (4.1.8) and write

$$\begin{aligned} H_0|\psi_{\pm}\rangle &= H_0 \frac{1}{\sqrt{2}} \left[|\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle \pm |\chi_{\alpha_1}^{(2)}\rangle \otimes |\chi_{\alpha_2}^{(1)}\rangle \right] \\ &= H_0^{(1)} \frac{1}{\sqrt{2}} \left[|\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle \pm |\chi_{\alpha_1}^{(2)}\rangle \otimes |\chi_{\alpha_2}^{(1)}\rangle \right] \\ &\quad + H_0^{(2)} \frac{1}{\sqrt{2}} \left[|\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle \pm |\chi_{\alpha_1}^{(2)}\rangle \otimes |\chi_{\alpha_2}^{(1)}\rangle \right] \\ &= \frac{1}{\sqrt{2}} \left[E_{\alpha_1} |\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle \pm E_{\alpha_2} |\chi_{\alpha_1}^{(2)}\rangle \otimes |\chi_{\alpha_2}^{(1)}\rangle \right. \\ &\quad \left. + E_{\alpha_2} |\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle \pm E_{\alpha_1} |\chi_{\alpha_1}^{(2)}\rangle \otimes |\chi_{\alpha_2}^{(1)}\rangle \right] \\ &= (E_{\alpha_1} + E_{\alpha_2}) \frac{1}{\sqrt{2}} \left[|\chi_{\alpha_1}^{(1)}\rangle \otimes |\chi_{\alpha_2}^{(2)}\rangle \pm |\chi_{\alpha_1}^{(2)}\rangle \otimes |\chi_{\alpha_2}^{(1)}\rangle \right] \\ &= (E_{\alpha_1} + E_{\alpha_2}) |\psi_{\pm}\rangle \end{aligned} \quad (5.2.7)$$

The corresponding relation for $N > 2$ is proven in complete analogy.

The differences between bosons and fermions become most obvious for the ground state. Choosing the eigenstates $|\chi_{\alpha_i}\rangle$ of the single particle Hamiltonian such that the eigenvalues are ordered according to

$$E_0 \leq E_1 \leq E_2 \leq E_3 \leq \dots \quad (5.2.8)$$

we arrive at the ground state wave function

$$|\psi_{+}\rangle = \mathcal{S} |\chi_0^{(1)}\rangle \otimes |\chi_0^{(2)}\rangle \otimes \dots \otimes |\chi_0^{(N)}\rangle \quad , \quad (5.2.9)$$

where all particles accumulate in the single particle ground state and the energy (4.1.13) assumes the value $E = NE_0$.

In contrast, fermions have to obey the Pauli principle. The ground state thus must be completely different from the state (5.2.9) and we write

$$|\psi_{-}\rangle = \mathcal{A}|\chi_0^{(1)}\rangle \otimes |\chi_1^{(2)}\rangle \otimes \dots \otimes |\chi_{N-1}^{(N)}\rangle \quad , \quad (5.2.10)$$

with the total energy $E = \sum_{i=0}^{N-1} E_i$. This example already explains the well known arrangement of the electron shells in atoms as well as the systematics of the periodic table of the elements.

Still, the antisymmetric many-body state as given by Eqs. (5.2.3) to (5.2.5) seems to be not completely fixed since exchange of two rows or columns in Eq. (5.2.4) changes the sign of the Slater determinant. However, this ambiguity is fictitious and results if the antisymmetrization operator \mathcal{A} given in Eq. (5.1.17) is applied to an improperly specified direct product of single particle wave functions. In other words, we have to fix the order of single particle states and particles in the initial direct product (5.1.1), which itself is arbitrary, and only after that apply the antisymmetrization operator (5.1.17). Actually, such a fixed starting composition was implied throughout in Sec. 5.1. Just to be specific we complement the definition (5.1.1) by the standard convention $\alpha_1 \leq \alpha_2 \leq \dots \leq \alpha_N$, where now α_i labels single particle states, i.e. the index i labels different eigenstates not particles.

An important step forward now derives from the observation that, as a consequence of the totally symmetric and antisymmetric construction of the many-body wave function, it is completely characterized by the occupation number n_{α_i} of each of the single particle states $|\chi_{\alpha_i}\rangle$. The fundamental difference between bosons and fermions then translates into the requirement that the occupation numbers may assume the values

$$n_{\alpha} = 0, 1, 2, 3, \dots \quad \text{for bosons} \quad (5.2.11)$$

$$\text{and } n_{\alpha} = 0, 1 \quad \text{for fermions} \quad . \quad (5.2.12)$$

We are thus able to write Eqs. (5.2.1) and (5.2.3) in the compact form

$$|\{n\}\rangle = |n_0, n_1, n_2, \dots, n_{\alpha}, \dots\rangle \quad , \quad (5.2.13)$$

with the only restriction that the total number of particles must be fixed,

$$\sum_{\alpha=0}^{\infty} n_{\alpha} = N \quad . \quad (5.2.14)$$

With the occupation numbers at hand the normalization factors C_+ and C_- are easily calculated. To this end we assume the eigenstates $|\chi_{\alpha_i}\rangle$ of the single particle Hamiltonian to form a normalized and complete set within the single particle Hilbert space,

$$\langle \chi_{\alpha} | \chi_{\beta} \rangle = \delta_{\alpha\beta} \quad (5.2.15)$$

$$\sum_{\alpha} |\chi_{\alpha}\rangle \langle \chi_{\alpha}| = \mathcal{I} \quad \text{in } \mathcal{H}_1 \quad . \quad (5.2.16)$$

We then obtain for the square of the symmetric and antisymmetric wave function (5.2.1) and (5.2.3), respectively

$$\begin{aligned} 1 \stackrel{!}{=} \langle \psi_\epsilon | \psi_\epsilon \rangle &= C_\epsilon^2 \sum_{P \in S_N} \sum_{P' \in S_N} (\epsilon)^P (\epsilon)^{P'} \bigotimes_i^N \bigotimes_j^N \langle \chi_{\alpha_i} | \mathcal{P}_P^+ \mathcal{P}_{P'} | \chi_{\alpha_j} \rangle \\ &= N! C_\epsilon^2 \sum_{P' \in S_N} (\epsilon)^{P'} \bigotimes_i^N \bigotimes_j^N \langle \chi_{\alpha_i} | \mathcal{P}_{P'} | \chi_{\alpha_j} \rangle \quad , \end{aligned} \quad (5.2.17)$$

where $\epsilon = \pm 1$. For bosons ($\epsilon = +1$) there exist $n_\alpha!$ non-vanishing terms for each single particle state and we obtain for the normalization factor

$$C_+ = (N! n_0! n_1! \dots n_\alpha! \dots)^{-\frac{1}{2}} \quad . \quad (5.2.18)$$

In contrast, for fermions ($\epsilon = -1$) the only permutation resulting in a nonvanishing norm is the identity ($\epsilon^0 = 1$) and we arrive at the result

$$C_- = (N!)^{-\frac{1}{2}} \quad . \quad (5.2.19)$$

Eqs. (5.2.2) and (5.2.5) serve as illustrations. With the previous normalization factors the many-body states (5.2.13) form a normalized and complete set,

$$\langle n_0, n_1, \dots, n_\alpha, \dots | n'_0, n'_1, \dots, n'_\alpha, \dots \rangle = \delta_{n_0 n'_0} \delta_{n_1 n'_1} \delta_{n_\alpha n'_\alpha} \quad (5.2.20)$$

$$\sum_{\substack{\{n\} \\ n_\alpha = N}} |n_0, n_1, \dots, n_\alpha, \dots\rangle \langle n_0, n_1, \dots, n_\alpha, \dots| = \mathcal{I} \quad \text{in} \quad \mathcal{H}_N^{(\pm)} \quad . \quad (5.2.21)$$

Eventually, we omit the restriction Eq. (5.2.14) on the total number of particles and construct an extended Hilbert space by adding to the N -particle Hilbert spaces $\mathcal{H}_N^{(\pm)}$ the Hilbert space for 0 particles,

$$\mathcal{H}_0 = \{|0\rangle, \langle 0|0\rangle = 1, N = 0\} \quad , \quad (5.2.22)$$

which consists merely of the vacuum state $|0\rangle$. The direct sum of all these N -particle Hilbert spaces,

$$\mathcal{H}^{(\pm)} = \mathcal{H}_0 \oplus \mathcal{H}_1^{(\pm)} \oplus \mathcal{H}_2^{(\pm)} \oplus \dots \oplus \mathcal{H}_N^{(\pm)} \oplus \dots \quad , \quad (5.2.23)$$

with the condition that scalar products of states from different N -particle spaces vanish, is defined as the Fock space of a bosonic or fermionic system. In Fock space

$$\sum_{\{n\}} |\{n\}\rangle \langle \{n\}| = \mathcal{I} \quad \text{in} \quad \mathcal{H}^{(\pm)} \quad (5.2.24)$$

holds without any restriction for bosons and with the condition (5.2.12) for fermions, i.e.

$$\sum_{\{n\}} \dots = \begin{cases} \sum_{n_0=0}^{\infty} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \dots \sum_{n_\alpha=0}^{\infty} \dots & \text{in } \mathcal{H}^{(+)} \quad , \\ \sum_{n_0=0}^1 \sum_{n_1=0}^1 \sum_{n_2=0}^1 \dots \sum_{n_\alpha=0}^1 \dots & \text{in } \mathcal{H}^{(-)} \quad . \end{cases} \quad (5.2.25)$$

5.3 Creation and annihilation operators

Of course, transition from an N -particle Hilbert space $\mathcal{H}_N^{(\pm)}$ to its “neighbouring” Hilbert spaces $\mathcal{H}_{N\pm 1}^{(\pm)}$ can be accomplished only via creation or annihilation of particles. In the present section we will define the corresponding operators, which in Fock space play the role of ladder operators.

Concentrating on bosons first we define linear operators b_α^+ ($\alpha = 0, 1, 2, \dots$) acting in $\mathcal{H}^{(+)}$, which mediate the mapping from the Hilbert space $\mathcal{H}_N^{(+)}$ onto $\mathcal{H}_{N+1}^{(+)}$ via

$$b_\alpha^+ |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle = \sqrt{n_\alpha + 1} \cdot |n_0, n_1, n_2, \dots, n_\alpha + 1, \dots\rangle \quad . \quad (5.3.1)$$

Obviously, such “creation operators” create a particle in the single particle state $|\chi_\alpha\rangle$. We note, in particular, for the vacuum state

$$b_\alpha^+ |0\rangle = |0, 0, 0, \dots, n_\alpha = 1, \dots\rangle = |\chi_\alpha\rangle \quad . \quad (5.3.2)$$

Using Eq. (5.2.21) the adjoint operator of b_α^+ is found as

$$\begin{aligned} & b_\alpha |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle \\ &= \sum_{\{n'\}} |\{n'\}\rangle \langle \{n'\} | b_\alpha |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle \\ &= \sum_{\{n'\}} |\{n'\}\rangle [\langle n_0, n_1, n_2, \dots, n_\alpha, \dots | b_\alpha^+ |n'_0, n'_1, n'_2, \dots, n'_\alpha, \dots\rangle]^* \\ &= \sum_{\{n'\}} |n'_0, n'_1, n'_2, \dots, n'_\alpha, \dots\rangle \left[\delta_{n_0 n'_0} \delta_{n_1 n'_1} \dots \left(\delta_{n_\alpha n'_\alpha - 1} \sqrt{n'_\alpha + 1} \right) \dots \right] \quad . \end{aligned} \quad (5.3.3)$$

We thus note

$$b_\alpha |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle = \sqrt{n_\alpha} \cdot |n_0, n_1, n_2, \dots, n_\alpha - 1, \dots\rangle \quad . \quad (5.3.4)$$

Hence, the adjoint operator acts like an “annihilation operator” of a particle in the single particle state $|\chi_\alpha\rangle$. For the vacuum state we note especially

$$b_\alpha |0\rangle = 0 \quad \forall \alpha \quad . \quad (5.3.5)$$

Combining Eqs. (5.3.1) and (5.3.4) we obtain the result

$$b_\alpha^+ b_\alpha |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle = n_\alpha \cdot |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle \quad , \quad (5.3.6)$$

which gives rise to the definition of the self-adjoint occupation number operator

$$\hat{n}_\alpha = b_\alpha^+ b_\alpha = \hat{n}_\alpha^+ \quad , \quad (5.3.7)$$

as well as the operator of the total particle number

$$\hat{N} = \sum_{\alpha=0}^{\infty} \hat{n}_\alpha = \sum_{\alpha=0}^{\infty} b_\alpha^+ b_\alpha = \hat{N}^+ \quad . \quad (5.3.8)$$

Obviously the latter establishes the total particle number as a dynamic variable.

Combining Eqs. (5.3.2) and (5.3.4) in the way

$$b_\alpha b_\alpha^+ |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle = (n_\alpha + 1) \cdot |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle \quad (5.3.9)$$

and comparing to Eq. (5.3.6) we arrive at the commutation relation $b_\alpha b_\alpha^+ - b_\alpha^+ b_\alpha = \mathcal{I}$. In contrast, operators for different single particle states $\alpha \neq \beta$ commute and we note

$$[b_\alpha, b_\beta^+] = \delta_{\alpha\beta} \mathcal{I} \quad , \quad [b_\alpha, b_\beta] = [b_\alpha^+, b_\beta^+] = 0 \quad . \quad (5.3.10)$$

By successively applying creation operators to the vacuum state we are able to generate all the states (5.2.13). This leads to the single particle states $|\chi_\alpha\rangle$, then to two particle states (5.2.2),

$$\begin{aligned} b_\beta^+ b_\alpha^+ |0\rangle &= b_\beta^+ |0, 0, 0, \dots, n_\alpha = 1, \dots\rangle \\ &= \begin{cases} |0, 0, 0, \dots, n_\alpha = 1, \dots, n_\beta = 1, \dots\rangle & (\alpha < \beta) \\ \sqrt{2} |0, 0, 0, \dots, n_\alpha = 2, \dots\rangle & (\alpha = \beta) \end{cases} \\ &= \sqrt{1 + \delta_{\alpha\beta}} |\Phi_{\alpha\beta}\rangle \quad , \end{aligned} \quad (5.3.11)$$

and finally to all higher N -particle states

$$\begin{aligned} &\dots (b_\gamma^+)^{n_\gamma} \dots (b_\beta^+)^{n_\beta} (b_\alpha^+)^{n_\alpha} |0\rangle \Big|_{\sum n_\alpha = N} \\ &= (n_0! n_1! \dots n_\alpha! \dots)^{\frac{1}{2}} |n_0, n_1, \dots, n_\alpha, \dots\rangle \Big|_{\sum n_\alpha = N} \quad . \end{aligned} \quad (5.3.12)$$

However, there exist $N!$ ways of arranging the creation operators of an N -particle state, which, according to the commutation relation (5.3.10) are all equivalent and due to the antisymmetrization generate $\frac{N!}{n_0! n_1! \dots n_\alpha! \dots}$ different states. Thus, in order to avoid such an ‘‘overcomplete’’ set, which would violate the normalization, we restrict the possible arrangements of creation operators to only a single one and choose as already proposed in Sec. 5.2 the conventional set characterized by $\alpha_1 \leq \alpha_2 \leq \dots \leq \alpha_N$, where groups of equal α_i and α_j may be combined.

Turning to the fermion case we proceed in a similar way as for bosons but have to take care of the antisymmetry of the many-body state. This is achieved by defining the creation operator as

$$\begin{aligned} a_\alpha^+ |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle \\ &= \eta_\alpha \sqrt{n_\alpha + 1} \cdot |n_0, n_1, n_2, \dots, n_\alpha + 1, \dots\rangle \\ &= \eta_\alpha \delta_{n_\alpha 0} |n_0, n_1, n_2, \dots, n_\alpha + 1, \dots\rangle \quad , \end{aligned} \quad (5.3.13)$$

where the phase factors are given by

$$\eta_\alpha = (-1)^{\left(\sum_{\beta=0}^{\alpha-1} n_\beta\right)} \quad . \quad (5.3.14)$$

Note that these phase factors again imply a certain, arbitrarily preselected ordering of the single particle states. As for bosons the adjoint operators,

$$\begin{aligned} & a_\alpha |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle \\ &= \eta_\alpha \sqrt{n_\alpha} \cdot |n_0, n_1, n_2, \dots, n_\alpha - 1, \dots\rangle \\ &= \eta_\alpha \delta_{n_\alpha 1} |n_0, n_1, n_2, \dots, n_\alpha - 1, \dots\rangle \quad , \end{aligned} \quad (5.3.15)$$

annihilate particles and we note especially for the vacuum state

$$a_\alpha |0\rangle = 0 \quad \forall \alpha \quad . \quad (5.3.16)$$

In Eqs. (5.3.13) and (5.3.15) we omitted in the respective second lines the square root factors thus accounting for the fermion condition (5.2.12). Since $\eta_\alpha^2 = 1$ and $\delta_{n_\alpha 1} = n_\alpha$ for $n_\alpha = 0, 1$ we are able to define the self-adjoint occupation number operators

$$\hat{n}_\alpha = a_\alpha^+ a_\alpha = \hat{n}_\alpha^+ \quad , \quad (5.3.17)$$

with

$$\hat{n}_\alpha |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle = n_\alpha \cdot |n_0, n_1, n_2, \dots, n_\alpha, \dots\rangle \quad , \quad (5.3.18)$$

as well as the operator of the total particle number

$$\hat{N} = \sum_{\alpha=0}^{\infty} \hat{n}_\alpha = \sum_{\alpha=0}^{\infty} a_\alpha^+ a_\alpha = \hat{N}^- \quad (5.3.19)$$

in the same manner as for bosons above.

In order to derive commutation relations for the just defined fermion operators we compare (for $\alpha < \beta$)

$$\begin{aligned} & a_\beta^+ a_\alpha^+ |n_0, n_1, n_2, \dots, n_\alpha, \dots, n_\beta, \dots\rangle \\ &= a_\beta^+ (\eta_\alpha \sqrt{n_\alpha + 1}) \cdot |n_0, n_1, n_2, \dots, n_\alpha + 1, \dots, n_\beta, \dots\rangle \\ &= (\eta'_\beta \sqrt{n_\beta + 1}) \cdot (\eta_\alpha \sqrt{n_\alpha + 1}) \cdot |n_0, n_1, n_2, \dots, n_\alpha + 1, \dots, n_\beta + 1, \dots\rangle \end{aligned} \quad (5.3.20)$$

with

$$\begin{aligned} & a_\alpha^+ a_\beta^+ |n_0, n_1, n_2, \dots, n_\alpha, \dots, n_\beta, \dots\rangle \\ &= a_\alpha^+ (\eta_\beta \sqrt{n_\beta + 1}) \cdot |n_0, n_1, n_2, \dots, n_\alpha, \dots, n_\beta + 1, \dots\rangle \\ &= (\eta_\alpha \sqrt{n_\alpha + 1}) \cdot (\eta_\beta \sqrt{n_\beta + 1}) \cdot |n_0, n_1, n_2, \dots, n_\alpha + 1, \dots, n_\beta + 1, \dots\rangle \quad . \end{aligned} \quad (5.3.21)$$

According to Eq. (5.3.14) we have $\eta'_\beta = -\eta_\beta$ since η'_β is built with $n_\alpha + 1$. We thus note the general result

$$a_\beta^+ a_\alpha^+ |\{n\}\rangle = -a_\alpha^+ a_\beta^+ |\{n\}\rangle \quad \text{for } \alpha \neq \beta \quad , \quad (5.3.22)$$

which represents the antisymmetry of the many-body wave function with respect to exchange of two particles. Since Eq. (5.3.22) is valid for all many-body states we note the operator identity

$$a_{\beta}^{\dagger} a_{\alpha}^{\dagger} + a_{\alpha}^{\dagger} a_{\beta}^{\dagger} = 0 \quad , \quad (5.3.23)$$

which, for $\alpha = \beta$, reduces to a different formulation of the Pauli principle,

$$(a_{\alpha}^{\dagger})^2 = 0 \quad \forall \alpha \quad . \quad (5.3.24)$$

For a pair of annihilators we note in complete analogy (for $\alpha \neq \beta$)

$$\begin{aligned} & a_{\beta} a_{\alpha} |n_0, n_1, n_2, \dots, n_{\alpha}, \dots, n_{\beta}, \dots\rangle \\ &= a_{\beta} (\eta_{\alpha} \sqrt{n_{\alpha}}) \cdot |n_0, n_1, n_2, \dots, n_{\alpha} - 1, \dots, n_{\beta}, \dots\rangle \\ &= (\eta'_{\beta} \sqrt{n_{\beta}}) \cdot (\eta_{\alpha} \sqrt{n_{\alpha}}) \cdot |n_0, n_1, n_2, \dots, n_{\alpha} - 1, \dots, n_{\beta} - 1, \dots\rangle \end{aligned} \quad (5.3.25)$$

with

$$\begin{aligned} & a_{\alpha} a_{\beta} |n_0, n_1, n_2, \dots, n_{\alpha}, \dots, n_{\beta}, \dots\rangle \\ &= a_{\alpha} (\eta_{\beta} \sqrt{n_{\beta}}) \cdot |n_0, n_1, n_2, \dots, n_{\alpha}, \dots, n_{\beta} - 1, \dots\rangle \\ &= (\eta_{\alpha} \sqrt{n_{\alpha}}) \cdot (\eta_{\beta} \sqrt{n_{\beta}}) \cdot |n_0, n_1, n_2, \dots, n_{\alpha} - 1, \dots, n_{\beta} - 1, \dots\rangle \quad . \end{aligned} \quad (5.3.26)$$

Now, η'_{β} is built with $n_{\alpha} - 1$, hence, we have according to Eq. (5.3.14) $\eta'_{\beta} = -\eta_{\beta}$ and note the operator identity

$$a_{\beta} a_{\alpha} + a_{\alpha} a_{\beta} = 0 \quad , \quad (5.3.27)$$

which, for $\alpha = \beta$, reduces to

$$(a_{\alpha})^2 = 0 \quad \forall \alpha \quad . \quad (5.3.28)$$

Finally, the relation for a pair of a creator and an annihilator (for $\alpha \neq \beta$) can be derived along the same lines and results in

$$a_{\beta}^{\dagger} a_{\alpha} + a_{\alpha} a_{\beta}^{\dagger} = 0 \quad . \quad (5.3.29)$$

However, for $\alpha = \beta$ the situation changes completely. Using Eqs. (5.3.13) and (5.3.15) we write

$$\begin{aligned} & [a_{\alpha}^{\dagger} a_{\alpha} + a_{\alpha} a_{\alpha}^{\dagger}] |n_0, n_1, n_2, \dots, n_{\alpha}, \dots\rangle \\ &= \eta_{\alpha}^2 [\delta_{n_{\alpha}-1,0} \delta_{n_{\alpha},1} + \delta_{n_{\alpha}+1,1} \delta_{n_{\alpha},0}] |n_0, n_1, n_2, \dots, n_{\alpha} - 1, \dots\rangle \\ &= |n_0, n_1, n_2, \dots, n_{\alpha} - 1, \dots\rangle \quad , \end{aligned} \quad (5.3.30)$$

which leads to the operator identity

$$a_{\alpha}^{\dagger} a_{\alpha} + a_{\alpha} a_{\alpha}^{\dagger} = \mathcal{I} \quad . \quad (5.3.31)$$

Defining the anticommutator of two operators by

$$\{A, B\} := AB + BA \quad (5.3.32)$$

we may thus combine the previous results to the effect

$$\{a_\alpha, a_\beta^+\} = \delta_{\alpha\beta} \mathcal{I} \quad , \quad \{a_\alpha, a_\beta\} = \{a_\alpha^+, a_\beta^+\} = 0 \quad , \quad (5.3.33)$$

which is the analogon to Eq. (5.3.10).

As for the boson case we are able to construct any many-body fermion state by successively applying creation operators to the vacuum state

$$a_N^+ \cdots a_2 a_1^+ |0\rangle \Big|_{\sum_{n_\alpha} = N} = |n_0, n_1, \dots, n_\alpha, \dots\rangle \Big|_{\sum_{n_\alpha} = N} \quad , \quad (5.3.34)$$

again with the convention to use only those arrangements of operators, which fulfil $\alpha_1 \leq \alpha_2 \leq \dots \leq \alpha_N$.

By now, our description of a system of identical particles has started to change away from a representation in terms of single particle states as well as their symmetrized and antisymmetrized direct products, Eqs. (5.2.1) and (5.2.3), towards a new language based on creation and annihilation operators. The latter usually goes under the terms “second quantization” or, more correctly, “occupation number representation”. This new and very efficient formalism avoids the complicated handling of many-body wave functions including the counting of single particle occupations. Furthermore, the explicit symmetrization and antisymmetrization, respectively, of the direct products (5.1.1) are hidden behind the conceptually much simpler commutator and anticommutator relations (5.3.10) and (5.3.33).

5.4 Representation of operators

In order to extend the very comfortable formalism provided by the definition of creation and annihilation operators we will next express all physical observables in terms of these somewhat “fundamental” operators. A first step into this direction was already done by defining the occupation number operators (5.3.7) and (5.3.17) as well as the total particle number operators (5.3.8) and (5.3.19) for bosons and fermions, respectively.

In generalizing the notions of the previous section to other operators we use the Hamiltonian (4.1.6) as a guideline. As already discussed in Sec. 4.1 this operator falls into a sum of single particle operators plus a double sum over operators acting on a pair of particles. Starting with the first term we write the general single particle operator in analogy to Eq. (4.1.8) as

$$F^{(N)} = \sum_i^N f^{(i)} \quad \text{with} \quad (f^{(i)})^+ = f^{(i)} \quad , \quad (5.4.1)$$

where we have assumed an N -particle system. However, this is no restriction at all since the operators of interest here conserve the number of particles. Using

the eigenstates $|\chi_{\alpha_i}\rangle$ of the single particle Hamiltonian, which, according to Eqs. (5.2.15) and (5.2.16), form a normalized and complete set within the single particle Hilbert space, we express the operator F in terms of the matrix elements

$$\langle \chi_{\alpha}^{(i)} | f^{(i)} | \chi_{\beta}^{(i)} \rangle = \langle \chi_{\alpha} | f | \chi_{\beta} \rangle = f_{\alpha\beta} \quad , \quad (5.4.2)$$

which, of course, are the same for all particles, hence, act in the same way in all single particle Hilbert spaces \mathcal{H}_i , as

$$\begin{aligned} F^{(N)} &= \sum_i^N \sum_{\alpha\beta} |\chi_{\alpha}^{(i)}\rangle \langle \chi_{\alpha}^{(i)}| f^{(i)} |\chi_{\beta}^{(i)}\rangle \langle \chi_{\beta}^{(i)}| \\ &= \sum_{\alpha\beta} \langle \chi_{\alpha} | f | \chi_{\beta} \rangle \cdot \left[\sum_i^N |\chi_{\alpha}^{(i)}\rangle \langle \chi_{\beta}^{(i)}| \right] \quad . \end{aligned} \quad (5.4.3)$$

Next we apply this operator to the general N -particle boson state (5.2.1). If $j_1, j_2, \dots, j_{n_{\beta}}$ are those n_{β} particles, which occupy the single particle state $|\chi_{\beta}^{(i)}\rangle$, we arrive at

$$\begin{aligned} &\sum_i^N |\chi_{\alpha}^{(i)}\rangle \langle \chi_{\beta}^{(i)}| \cdot |\psi_{+}\rangle \\ &= \sum_i^N |\chi_{\alpha}^{(i)}\rangle \langle \chi_{\beta}^{(i)}| \\ &\quad \cdot \left[C_{+}(\{n\}) \sum_{P \in S_N} \mathcal{P}_P \left[\dots \otimes |\chi_{\beta}^{(j_1)}\rangle \otimes |\chi_{\beta}^{(j_2)}\rangle \otimes \dots \otimes |\chi_{\beta}^{(j_{n_{\beta}})}\rangle \otimes \dots \right] \right] \\ &= C_{+}(\{n\}) \sum_{P \in S_N} \mathcal{P}_P \left[\dots \otimes |\chi_{\alpha}^{(j_1)}\rangle \otimes |\chi_{\beta}^{(j_2)}\rangle \otimes \dots \otimes |\chi_{\beta}^{(j_{n_{\beta}})}\rangle \otimes \dots \right. \\ &\quad \left. + \dots \otimes |\chi_{\beta}^{(j_1)}\rangle \otimes |\chi_{\alpha}^{(j_2)}\rangle \otimes \dots \otimes |\chi_{\beta}^{(j_{n_{\beta}})}\rangle \otimes \dots \right. \\ &\quad \left. + \dots \otimes |\chi_{\beta}^{(j_1)}\rangle \otimes |\chi_{\beta}^{(j_2)}\rangle \otimes \dots \otimes |\chi_{\alpha}^{(j_{n_{\beta}})}\rangle \otimes \dots \right] \quad . \end{aligned} \quad (5.4.4)$$

We thus end up with exactly n_{β} terms within the square brackets. All other terms vanish due to the orthonormalization of the single particle states, Eq. (5.2.15). After symmetrization we obtain, apart from the normalization, the states $|\dots n_{\alpha}+1 \dots n_{\beta}-1 \dots\rangle$ and $|\dots n_{\beta} \dots\rangle$ for $\alpha \neq \beta$ and $\alpha = \beta$, respectively. Finally, accounting for the boson normalization factor given by Eq. (5.2.18) we arrive at the result

$$\sum_i^N |\chi_{\alpha}^{(i)}\rangle \langle \chi_{\beta}^{(i)}| \cdot |\psi_{+}\rangle$$

$$\begin{aligned}
&= n_\beta \cdot \begin{cases} \frac{C_+(\dots n_\alpha \dots n_\beta \dots)}{C_+(\dots n_\alpha + 1 \dots n_\beta - 1 \dots)} |\dots n_\alpha + 1 \dots n_\beta - 1 \dots\rangle & \text{for } \alpha \neq \beta \\ |\dots n_\beta \dots\rangle & \text{for } \alpha = \beta \end{cases} \\
&= \begin{cases} \sqrt{(n_\alpha + 1)n_\beta} \cdot |\dots n_\alpha + 1 \dots n_\beta - 1 \dots\rangle & \text{for } \alpha \neq \beta \\ n_\beta \cdot |\dots n_\beta \dots\rangle & \text{for } \alpha = \beta \end{cases} \quad (5.4.5)
\end{aligned}$$

Since the previous derivation holds for any N -particle boson state, we may, comparing to Eqs. (5.3.1), (5.3.4), (5.3.6), and (5.3.7), summarize it to the following operator identity

$$\sum_i^N |\chi_\alpha^{(i)}\rangle \langle \chi_\beta^{(i)}| = b_\alpha^+ b_\beta | \mathcal{H}_N^{(+)} \quad (5.4.6)$$

For fermions we proceed in much the same manner, remembering, however, that each single particle state can be either empty or singly occupied. We then obtain instead of Eq. (5.4.4)

$$\begin{aligned}
&\sum_i^N |\chi_\alpha^{(i)}\rangle \langle \chi_\beta^{(i)}| \cdot |\psi_-\rangle \\
&= \sum_i^N |\chi_\alpha^{(i)}\rangle \langle \chi_\beta^{(i)}| \cdot \left[C_-(\{n\}) \sum_{P \in S_N} (-)^P \mathcal{P}_P \left[\dots \otimes |\chi_\beta^{(j)}\rangle \otimes \dots \right] \right] \\
&= \delta_{n_\beta 1} C_-(\{n\}) \sum_{P \in S_N} (-)^P \mathcal{P}_P \left[\dots \otimes |\chi_\alpha^{(j)}\rangle \otimes \dots \right] \quad , \quad (5.4.7)
\end{aligned}$$

where the prefactor $\delta_{n_\beta 1}$ accounts for the occupation 0 or 1 of the single particle state $|\chi_\beta\rangle$. For $\alpha = \beta$ the state $|\psi_-\rangle$ has thus simply been reproduced. In contrast, for $\alpha \neq \beta$ it may still happen that the single particle state $|\chi_\alpha\rangle$ was already occupied before. In this case we must end up with the zero vector on the right hand side of Eq. (5.4.7), which can be achieved by multiplying with $\delta_{n_\alpha 0}$. However, if the single particle state $|\chi_\alpha\rangle$ was empty before we obtain the result $|\dots n_\alpha + 1 \dots n_\beta - 1 \dots\rangle$ on the right hand side of Eq. (5.4.7) apart from additional phase factors taking care of the correct position of the state within the direct product. In order to bring the single particle state to the right position we will need

$$\sum_{\gamma}^{\beta-1} n_\gamma - \sum_{\gamma}^{\alpha-1} n_\gamma$$

transpositions, which corresponds to a prefactor $\eta_\alpha \cdot \eta_\beta$. Summarizing we arrive at

$$\begin{aligned}
&\sum_i^N |\chi_\alpha^{(i)}\rangle \langle \chi_\beta^{(i)}| \cdot |\psi_-\rangle \\
&= \begin{cases} \delta_{n_\alpha 0} \delta_{n_\beta 1} \eta_\alpha \eta_\beta \cdot |\dots n_\alpha + 1 \dots n_\beta - 1 \dots\rangle & \text{for } \alpha \neq \beta \\ n_\beta \cdot |\dots n_\beta \dots\rangle & \text{for } \alpha = \beta \end{cases} \quad , \quad (5.4.8)
\end{aligned}$$

where we have used the identity $\delta_{n_\beta 1} = n_\beta$ for $n_\beta = 0, 1$ in the second line. Since the previous derivation holds for any N -particle fermion state, we obtain, comparing to Eqs. (5.3.13), (5.3.15), and (5.3.17), the operator identity

$$\sum_i^N |\chi_\alpha^{(i)}\rangle\langle\chi_\beta^{(i)}| = a_\alpha^+ a_\beta \Big|_{\mathcal{H}_N^{(-)}} \quad . \quad (5.4.9)$$

Finally, combining Eqs. (5.4.3), (5.4.6), and (5.4.9), we identify the single particle operator $F^{(N)}$ of Eq. (5.4.1) as the restriction of the more general single particle operator

$$F = \sum_{\alpha\beta} \langle\chi_\alpha|f|\chi_\beta\rangle b_\alpha^+ b_\beta \quad \text{for bosons} \quad (5.4.10)$$

$$F = \sum_{\alpha\beta} \langle\chi_\alpha|f|\chi_\beta\rangle a_\alpha^+ a_\beta \quad \text{for fermions} \quad (5.4.11)$$

to the N -particle Hilbert spaces $\mathcal{H}_N^{(+)}$ and $\mathcal{H}_N^{(-)}$. In contrast, the operator F is independent of the particle number N and acts in Fock space.

As already mentioned, most simple examples of a single particle operator are the total particle number operators (5.3.8) and (5.3.19) for bosons and fermions, respectively. Comparing Eqs. (5.4.10) and (5.4.11) to Eqs. (5.3.8) and (5.3.19) we note

$$\langle\chi_\alpha|\hat{n}|\chi_\beta\rangle = \delta_{\alpha\beta} \quad \iff \quad \hat{n} = \mathcal{I} \quad . \quad (5.4.12)$$

Another example is the one-particle contribution to the Hamiltonian (4.1.6), which can now be written as

$$H_0^{\{1\}} = \sum_{\alpha\beta} \langle\chi_\alpha| \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} |\chi_\beta\rangle a_\alpha^+ a_\beta \quad . \quad (5.4.13)$$

Within the independent electron approximation, Eqs. (4.1.8)/(4.1.9), this term approximates the full Hamiltonian, which assumes the form

$$H_0 = \sum_\alpha E_\alpha a_\alpha^+ a_\alpha = \sum_\alpha E_\alpha \hat{n}_\alpha \quad . \quad (5.4.14)$$

Here we have used Schrödinger's equation (4.1.11) as well as the orthonormalization of the single particle states according to Eq. (5.2.15).

Next we turn to the two-particle operators, which, for an N -particle system, assume the general form

$$\begin{aligned} G^{(N)} &= \frac{1}{2} \sum_{\substack{i,j \\ j \neq i}}^N g^{(i,j)} \\ &= \frac{1}{2} \sum_{i,j}^N (1 - \delta_{ij}) g^{(i,j)} \quad \text{with} \quad (g^{(i,j)})^+ = g^{(i,j)} \\ &\quad \text{and} \quad (g^{(j,i)}) = g^{(i,j)} \quad , \quad (5.4.15) \end{aligned}$$

which acts on the two-particle Hilbert space $\mathcal{H}_i \otimes \mathcal{H}_j$. An example for such an operator is the electron-electron interaction as given by the last term of Eq. (4.1.6). In Eq. (5.4.15) we have in the second line added an alternative writing, which suggests to first calculate $g^{(i,j)}$ for arbitrary i and j and after that to subtract the “diagonal” interaction term $g^{(i,i)}$, which comprises the erroneous interaction of a particle with itself. However, unfortunately such a stepwise procedure is not possible for the Coulomb potential

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

due to its divergence for $\mathbf{r}_i = \mathbf{r}_j$. In this case we start from a modified Coulomb potential

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j| + a} \quad ,$$

calculate the matrix elements of $g^{(i,j)}$ for arbitrary i and j , and, after having subtracted $g^{(i,i)}$, perform the limit $a \rightarrow 0$.

We may now follow the same line as for single particle operators above and, using the general matrix element,

$$\left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} g^{(1,2)} \left\{ | \chi_\beta^{(1)} \rangle \otimes | \chi_\delta^{(2)} \rangle \right\} = g_{\alpha\gamma, \beta\delta} \quad , \quad (5.4.16)$$

as well as the closure relation (5.2.16), express the operator $g^{(i,j)}$ as

$$\begin{aligned} G^{(N)} &= \frac{1}{2} \sum_{i,j} (1 - \delta_{ij}) \sum_{\alpha\gamma} \sum_{\beta\delta} \left\{ | \chi_\alpha^{(i)} \rangle \otimes | \chi_\gamma^{(j)} \rangle \right\} \left\{ \langle \chi_\alpha^{(i)} | \otimes \langle \chi_\gamma^{(j)} | \right\} \\ &\quad g^{(i,j)} \left\{ | \chi_\beta^{(i)} \rangle \otimes | \chi_\delta^{(j)} \rangle \right\} \left\{ \langle \chi_\beta^{(i)} | \otimes \langle \chi_\delta^{(j)} | \right\} \\ &= \frac{1}{2} \sum_{\alpha\gamma} \sum_{\beta\delta} g_{\alpha\gamma, \beta\delta} \\ &\quad \cdot \left\{ \left[\sum_j^N | \chi_\gamma^{(j)} \rangle \langle \chi_\delta^{(j)} | \right] \left[\sum_i^N | \chi_\alpha^{(i)} \rangle \langle \chi_\beta^{(i)} | \right] - \delta_{\delta\alpha} \left[\sum_i^N | \chi_\gamma^{(i)} \rangle \langle \chi_\beta^{(i)} | \right] \right\} \quad , \end{aligned} \quad (5.4.17)$$

where we have used the identity

$$\delta_{ij} \langle \chi_\delta^{(i)} | \chi_\alpha^{(j)} \rangle = \delta_{ij} \delta_{\delta\alpha} \quad . \quad (5.4.18)$$

With the help of Eqs. (5.4.6) and (5.4.9) this intermediate result can be easily expressed by creation and annihilation operators and we obtain for bosons

$$G^{(N)} = \frac{1}{2} \sum_{\alpha\gamma} \sum_{\beta\delta} g_{\alpha\gamma, \beta\delta} \cdot \left\{ (b_\gamma^+ b_\delta) (b_\alpha^+ b_\beta) - \delta_{\delta\alpha} (b_\gamma^+ b_\beta) \right\} \quad , \quad (5.4.19)$$

Using the commutation relations (5.3.10) we rewrite the term in curly brackets as

$$\begin{aligned}
(b_\gamma^+ b_\delta) (b_\alpha^+ b_\beta) - \delta_{\delta\alpha} (b_\gamma^+ b_\beta) &= b_\gamma^+ [b_\delta b_\alpha^+ - \delta_{\delta\alpha} \mathcal{I}] b_\beta \\
&= b_\gamma^+ b_\alpha^+ b_\delta b_\beta \\
&= b_\alpha^+ b_\gamma^+ b_\delta b_\beta \quad . \quad (5.4.20)
\end{aligned}$$

In contrast, for fermions we obtain

$$\begin{aligned}
(a_\gamma^+ a_\delta) (a_\alpha^+ a_\beta) - \delta_{\delta\alpha} (a_\gamma^+ a_\beta) &= a_\gamma^+ [a_\delta a_\alpha^+ - \delta_{\delta\alpha} \mathcal{I}] a_\beta \\
&= a_\gamma^+ (-a_\alpha^+ a_\delta) a_\beta \\
&= a_\alpha^+ a_\gamma^+ a_\delta a_\beta \quad . \quad (5.4.21)
\end{aligned}$$

Note that the exclusion of the self-interaction of a particle, which led to the second term in Eqs. (5.4.17) and (5.4.19), has translated into the order of creation and annihilation operators in Eqs. (5.4.20) and (5.4.21). While in these two equations in the first term on the left hand side one of the interacting particles is annihilated and created and only after that the same is done for the second particle, the term on the right hand side acts in a completely different way. Here, both particles are annihilated before they both are created. Thus the suppression of the self-interaction is completely covered by the formalism and, most important, needs not be explicitly accounted for by additional Kronecker δ 's.

Finally, combining these expressions with Eq. (5.4.19) we arrive at the following result for the general two-particle operator in Fock space,

$$G = \frac{1}{2} \sum_{\alpha\gamma} \sum_{\beta\delta} \left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} g^{(1,2)} \left\{ | \chi_\beta^{(1)} \rangle \otimes | \chi_\delta^{(2)} \rangle \right\} b_\alpha^+ b_\gamma^+ b_\delta b_\beta \quad \text{for bosons} \quad (5.4.22)$$

$$G = \frac{1}{2} \sum_{\alpha\gamma} \sum_{\beta\delta} \left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} g^{(1,2)} \left\{ | \chi_\beta^{(1)} \rangle \otimes | \chi_\delta^{(2)} \rangle \right\} a_\alpha^+ a_\gamma^+ a_\delta a_\beta \quad \text{for fermions} \quad , \quad (5.4.23)$$

which goes beyond Eq. (5.4.15) defined within the N -particle Hilbert spaces $\mathcal{H}_N^{(+)}$ and $\mathcal{H}_N^{(-)}$. Note the order of annihilation operators in Eqs. (5.4.22) and (5.4.23)!

As an example we refer to the electron-electron interaction term entering the Hamiltonian (4.1.6), which now assumes the form

$$H_0^{\{2\}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} = \frac{1}{2} \sum_{\alpha\gamma} \sum_{\beta\delta} v_{\alpha\gamma,\beta\delta}^{(el-el)} a_\alpha^+ a_\gamma^+ a_\delta a_\beta \quad , \quad (5.4.24)$$

with

$$v_{\alpha\gamma,\beta\delta}^{(el-el)} = \frac{1}{4\pi\epsilon_0} \left\{ \langle \chi_\alpha^{(i)} | \otimes \langle \chi_\gamma^{(j)} | \right\} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \left\{ | \chi_\beta^{(i)} \rangle \otimes | \chi_\delta^{(j)} \rangle \right\} \quad . \quad (5.4.25)$$

Just for completeness we combine Eqs. (5.4.13), (5.4.24) as well as (5.4.25) and write the full electronic Hamiltonian (4.1.6) as

$$\begin{aligned}
H_0 &= \sum_{\alpha\beta} \langle \chi_\alpha | \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} | \chi_\beta \rangle a_\alpha^\dagger a_\beta \\
&\quad + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\alpha\gamma} \sum_{\beta\delta} \left\{ \langle \chi_\alpha^{(i)} | \otimes \langle \chi_\gamma^{(j)} | \right\} \\
&\quad \quad \quad \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \left\{ | \chi_\beta^{(i)} \rangle \otimes | \chi_\delta^{(j)} \rangle \right\} a_\alpha^\dagger a_\gamma^\dagger a_\delta a_\beta \quad .
\end{aligned} \tag{5.4.26}$$

Of course, the just described construction of one- and two-particle operators in Fock space can be straightforwardly extended to many particle operators.

5.5 Reduced density matrices

As a matter of fact most observables of interest grow out of one or two particle operators as given by Eqs. (5.4.1) and (5.4.15), which we expressed in the previous section in terms of creation and annihilation operators in Eqs. (5.4.10)/(5.4.11) as well as (5.4.22)/(5.4.23). In order to calculate expectation values of these operators we thus have to calculate

$$\begin{aligned}
\langle F \rangle &= Tr(WF) \\
&= \sum_{\alpha\beta} \langle \chi_\alpha | f | \chi_\beta \rangle Tr(W b_\alpha^\dagger b_\beta) \quad ,
\end{aligned} \tag{5.5.1}$$

$$\begin{aligned}
\langle G \rangle &= Tr(WG) \\
&= \frac{1}{2} \sum_{\alpha\gamma} \sum_{\beta\delta} \left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} g^{(1,2)} \left\{ | \chi_\beta^{(1)} \rangle \otimes | \chi_\delta^{(2)} \rangle \right\} \\
&\quad \quad \quad \cdot Tr(W b_\alpha^\dagger b_\gamma^\dagger b_\delta b_\beta) \quad ,
\end{aligned} \tag{5.5.2}$$

where W is the full density matrix characterizing the many-body state and the trace Tr denotes the sum of the diagonal elements as usual. As is obvious from Eqs. (5.5.1) and (5.5.2) this requires to evaluate the so-called reduced density matrices

$$\rho_1(\beta; \alpha) = Tr(W b_\alpha^\dagger b_\beta) \quad , \tag{5.5.3}$$

$$\rho_2(\beta\delta; \alpha\gamma) = Tr(W b_\alpha^\dagger b_\gamma^\dagger b_\delta b_\beta) \quad ; \tag{5.5.4}$$

Eqs. (5.5.1) to (5.5.4) hold for both bosons and fermions. In particular at low temperatures, when the many-body system occupies the ground state $W = |\Psi_0\rangle\langle\Psi_0|$, we arrive at the reduced ground state density matrices

$$\rho_1^{(0)}(\beta; \alpha) = \langle \Psi_0 | b_\alpha^\dagger b_\beta | \Psi_0 \rangle \quad , \tag{5.5.5}$$

$$\rho_2^{(0)}(\beta\delta; \alpha\gamma) = \langle \Psi_0 | b_\alpha^\dagger b_\gamma^\dagger b_\delta b_\beta | \Psi_0 \rangle \quad . \tag{5.5.6}$$

Having the reduced density matrices (5.5.3) and (5.5.4) at hand and using Eqs. (5.4.2) and (5.4.16) we express the expectation values (5.5.1) and (5.5.2) as

$$Tr(WF) = \sum_{\alpha\beta} f_{\alpha\beta} \cdot \rho_1(\beta; \alpha) = tr(f \cdot \rho_1) \quad , \quad (5.5.7)$$

$$Tr(WG) = \frac{1}{2} \sum_{\alpha\gamma} \sum_{\beta\delta} g_{\alpha\gamma, \beta\delta} \cdot \rho_2(\beta\delta; \alpha\gamma) = \frac{1}{2} tr(g \cdot \rho_2) \quad . \quad (5.5.8)$$

The normalizations of the reduced density matrices grow out of the previous relations with f and g replaced by the identity operator,

$$\begin{aligned} tr(\rho_1) &= \sum_{\alpha} \rho_1(\alpha; \alpha) = \sum_{\alpha} Tr(Wb_{\alpha}^{+}b_{\beta}) = Tr(W\hat{N}) \\ &= \langle \hat{N} \rangle \quad , \end{aligned} \quad (5.5.9)$$

$$\begin{aligned} tr(\rho_2) &= \sum_{\alpha\gamma} \rho_2(\alpha\gamma; \alpha\gamma) = \sum_{\alpha\gamma} Tr(Wb_{\alpha}^{+}b_{\gamma}^{+}b_{\gamma}b_{\alpha}) \\ &= Tr \left\{ W \sum_{\alpha\gamma} [(b_{\gamma}^{+}b_{\gamma})(b_{\alpha}^{+}b_{\alpha}) - \delta_{\alpha\gamma}(b_{\alpha}^{+}b_{\alpha})] \right\} \\ &= Tr \left\{ W \cdot [\hat{N}^2 - \hat{N}] \right\} \\ &= \langle \hat{N}^2 - \hat{N} \rangle = \langle \hat{N}(\hat{N} - \mathcal{I}) \rangle \quad , \end{aligned} \quad (5.5.10)$$

where we have used Eq. (5.4.20). All previous relations hold likewise for fermions, in which case we had to use Eq. (5.4.21).

According to Eqs. (5.5.7) and (5.5.8) the reduced one and two-particle density matrices contain less information and enable for a reduced calculational effort than the full density matrix W . This is due the fact that the reduced density matrices result from W by integrating over the degrees of freedom of all particles except for a single particle or two particles, respectively. At the same time the symmetry or antisymmetry of the respective many-body state are fully conserved.

In order to shed some more light onto the previous notions we discuss especially the reduced density matrices for the symmetrized and antisymmetrized pure many-body states (5.2.13), which we assume to be built from the orthonormalized eigenstates of the single particle Hamiltonian as resulting from the independent particle approximation. Using Eq. (5.3.15) we note for fermions

$$\begin{aligned} \rho_1^{\{n\}}(\beta; \alpha) &= \langle \{n\} | a_{\alpha}^{+} a_{\beta} | \{n\} \rangle \\ &= \langle a_{\alpha} \{n\} | a_{\beta} \{n\} \rangle \\ &= \eta_{\alpha} \eta_{\beta} \sqrt{n_{\alpha}} \sqrt{n_{\beta}} \delta_{\alpha\beta} \\ &= n_{\alpha} \delta_{\alpha\beta} \quad , \end{aligned} \quad (5.5.11)$$

since $\eta_{\alpha}^2 = 1$. The one particle reduced density matrix thus is a diagonal matrix with the occupation numbers being its eigenvalues. Summing over all diagonal

elemente we furthermore note

$$\text{tr} \rho_1 = N \quad . \quad (5.5.12)$$

Eqs. (5.5.11) and (5.5.12) hold likewise for bosons and fermions.

For the two-particle reduced density matrix we write in close analogy to Eq. (5.5.11)

$$\begin{aligned} \rho_2^{\{n\}}(\beta\delta; \alpha\gamma) &= \langle \{n\} | a_\alpha^+ a_\gamma^+ a_\delta a_\beta | \{n\} \rangle \\ &= \langle a_\gamma a_\alpha \{n\} | a_\delta a_\beta \{n\} \rangle \\ &= (1 - \delta_{\alpha\gamma})(1 - \delta_{\beta\delta}) \eta_\alpha \eta_\beta \sqrt{n_\alpha} \sqrt{n_\beta} \\ &\quad \langle a_\gamma(n_0 \dots n_\alpha - 1 \dots) | a_\delta(n_0 \dots n_\beta - 1 \dots) \rangle \end{aligned} \quad (5.5.13)$$

Two points are obvious from this formulation: First, for fermions we must have $\alpha \neq \gamma$ and $\beta \neq \delta$ as already expressed by the terms $(1 - \delta_{\dots})$. Second, in order that the scalar product does not vanish only two possibilities of arranging the indices of the annihilation operators remain, which lead to two different contributions. To be concrete, we note

$$\begin{aligned} \rho_2^{\{n\}}(\beta\delta; \alpha\gamma) &= (1 - \delta_{\alpha\gamma})(1 - \delta_{\beta\delta}) \eta_\alpha \eta_\beta \sqrt{n_\alpha} \sqrt{n_\beta} \\ &\quad \langle a_\gamma(n_0 \dots n_\alpha - 1 \dots) | a_\delta(n_0 \dots n_\beta - 1 \dots) \rangle \left[\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\delta} \delta_{\gamma\beta} \right] \\ &= (1 - \delta_{\alpha\gamma})(1 - \delta_{\beta\delta}) \\ &\quad \left[\delta_{\alpha\beta} \delta_{\gamma\delta} \eta_\alpha^2 n_\alpha \langle a_\gamma(n_0 \dots n_\alpha - 1 \dots) | a_\gamma(n_0 \dots n_\alpha - 1 \dots) \rangle \right. \\ &\quad \left. + \delta_{\alpha\delta} \delta_{\gamma\beta} \eta_\alpha \eta_\gamma \sqrt{n_\alpha} \sqrt{n_\gamma} \right. \\ &\quad \left. \langle a_\gamma(n_0 \dots n_\alpha - 1 \dots) | a_\alpha(n_0 \dots n_\gamma - 1 \dots) \rangle \right] \\ &= (1 - \delta_{\alpha\gamma}) \left[\delta_{\alpha\beta} \delta_{\gamma\delta} \eta_\alpha^2 n_\alpha (\eta'_\gamma)^2 n_\gamma + \delta_{\alpha\delta} \delta_{\gamma\beta} \eta_\alpha \eta_\gamma \eta'_\alpha \eta'_\gamma n_\alpha n_\gamma \right] \quad , \end{aligned} \quad (5.5.14)$$

where we have used the phase factors

$$\eta'_\gamma = \begin{cases} \eta_\gamma & \text{for } \gamma < \alpha \\ -\eta_\gamma & \text{for } \gamma > \alpha \end{cases} \quad , \quad (5.5.15)$$

$$\eta'_\alpha = \begin{cases} \eta_\alpha & \text{for } \alpha < \gamma \\ -\eta_\alpha & \text{for } \alpha > \gamma \end{cases} \quad . \quad (5.5.16)$$

In addition, we have omitted the term $(1 - \delta_{\beta\delta})$ in the last step of Eq. (5.5.14), since in combination with the Kronecker δ 's in the square bracket, $\beta = \delta$ is

equivalent to $\alpha = \gamma$. The values of the phase factors in Eqs. (5.5.15) and (5.5.16) depend on the arrangement of the single particle states with indices α and γ within the many-body state $|\{n\}\rangle$. In the first term of Eq. (5.5.14) both η_α^2 and $(\eta'_\gamma)^2$ contribute +1. In contrast, from Eqs. (5.5.15) and (5.5.16) we have

$$\eta'_\alpha \eta'_\gamma = -\eta_\alpha \eta_\gamma \quad (5.5.17)$$

due to the exchange of α and γ in the bra and ket state. We thus note

$$\rho_2^{\{n\}}(\beta\delta; \alpha\gamma) = (1 - \delta_{\alpha\gamma}) n_\alpha n_\gamma \left[\delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\delta} \delta_{\gamma\beta} \right] . \quad (5.5.18)$$

Finally omitting the $(1 - \delta_{\dots})$ factor, which is accounted for by the arrangement of Kronecker δ 's in the square bracket, we arrive at the result

$$\begin{aligned} \rho_2^{\{n\}}(\beta\delta; \alpha\gamma) &= n_\alpha n_\gamma \left[\delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\delta} \delta_{\gamma\beta} \right] \\ &= \rho_1^{\{n\}}(\beta; \alpha) \cdot \rho_1^{\{n\}}(\delta; \gamma) - \rho_1^{\{n\}}(\beta; \gamma) \cdot \rho_1^{\{n\}}(\delta; \alpha) . \end{aligned} \quad (5.5.19)$$

Due to the arrangement of the single particle indices the first and second contribution are called the direct and exchange term, respectively. Note that both terms fall into a product of reduced one particle density matrices, which fact is characteristic of ‘‘uncorrelated’’ many-body systems. Furthermore, we point out again that the suppression of the double occupancy for fermion systems, which we included by adding the $(1 - \delta_{\dots})$ factors above, is now implicit in the difference in the square brackets both in Eqs. (5.5.18) and (5.5.19), which vanishes for $\alpha = \gamma = \beta = \delta$. However, as we will see below it is useful to artificially include this matrix element in both terms within the square brackets.

For bosons the previous derivation can be adopted with two modifications. First, since all phase factors must be replaced by 1 we obtain a plus sign in the square bracket of Eqs. (5.5.18) and (5.5.19). Second, for bosons the cases $\alpha = \gamma$ and $\beta = \delta$ must be included and lead to an additional contribution. However, as is obvious from Eq. (5.5.13), for a nonvanishing scalar product $\alpha = \gamma$ actually implies not only $\beta = \delta$, but the equality of all four indices. With the help of Eq. (5.3.4) the additional term is thus easily calculated as

$$\begin{aligned} &\langle \{n\} | b_\alpha^+ b_\alpha^+ b_\alpha b_\alpha | \{n\} \rangle \\ &= \langle b_\alpha b_\alpha \{n\} | b_\alpha b_\alpha \{n\} \rangle \\ &= n_\alpha \langle b_\alpha(n_0 \dots n_\alpha - 1 \dots) | b_\alpha(n_0 \dots n_\alpha - 1 \dots) \rangle \\ &= n_\alpha(n_\alpha - 1) \langle (n_0 \dots n_\alpha - 2 \dots) | (n_0 \dots n_\alpha - 2 \dots) \rangle \end{aligned} \quad (5.5.20)$$

Now combining Eqs. (5.5.18) to (5.5.20) and taking into account the aforementioned modifications for bosons we note the result

$$\rho_2^{\{n\}}(\beta\delta; \alpha\gamma)$$

$$\begin{aligned}
&= (1 - \delta_{\alpha\gamma}) n_\alpha n_\gamma \left[\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\delta} \delta_{\gamma\beta} \right] + \delta_{\alpha\gamma} \delta_{\alpha\beta} \delta_{\gamma\delta} n_\alpha (n_\alpha - 1) \\
&= n_\alpha n_\gamma \left[\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\delta} \delta_{\gamma\beta} \right] + \delta_{\alpha\gamma} \delta_{\alpha\beta} \delta_{\gamma\delta} \{-2n_\alpha^2 + n_\alpha(n_\alpha - 1)\} \\
&= n_\alpha n_\gamma \left[\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\delta} \delta_{\gamma\beta} \right] - \delta_{\alpha\gamma} \delta_{\alpha\beta} \delta_{\gamma\delta} n_\alpha (n_\alpha + 1) \\
&= \rho_1^{\{n\}}(\beta; \alpha) \cdot \rho_1^{\{n\}}(\delta; \gamma) + \rho_1^{\{n\}}(\beta; \gamma) \cdot \rho_1^{\{n\}}(\delta; \alpha) \\
&\quad - \delta_{\alpha\gamma} \delta_{\alpha\beta} \delta_{\gamma\delta} \left[\left(\rho_1^{\{n\}}(\alpha; \beta) \right)^2 + \rho_1^{\{n\}}(\alpha; \beta) \right] . \tag{5.5.21}
\end{aligned}$$

As for fermions we thus have a direct and an exchange term, the latter now with a plus sign.

Inserting the expressions (5.5.11), (5.5.19), and (5.5.21) for the reduced density matrices into Eqs. (5.5.7) and (5.5.8) we obtain

$$\langle \{n\} | F | \{n\} \rangle = \sum_{\alpha} n_{\alpha} f_{\alpha\alpha} \quad , \tag{5.5.22}$$

valid for both bosons and fermions, as well as

$$\begin{aligned}
&\langle \{n\} | G | \{n\} \rangle \\
&= \frac{1}{2} \sum_{\alpha\gamma} n_{\alpha} n_{\gamma} \left[g_{\alpha\gamma, \alpha\gamma} - g_{\alpha\gamma, \gamma\alpha} \right] \quad \text{for fermions} \quad , \tag{5.5.23}
\end{aligned}$$

$$\begin{aligned}
&\langle \{n\} | G | \{n\} \rangle \\
&= \frac{1}{2} \sum_{\alpha\gamma} \left\{ n_{\alpha} n_{\gamma} \left[g_{\alpha\gamma, \alpha\gamma} + g_{\alpha\gamma, \gamma\alpha} \right] - \delta_{\alpha\gamma} n_{\alpha} (n_{\alpha} + 1) g_{\alpha\alpha, \alpha\alpha} \right\} \\
&\quad \text{for bosons} \quad , \tag{5.5.24}
\end{aligned}$$

In particular for the ground state $|\Psi_0\rangle$, which for bosons is characterized by

$$|\{n\}\rangle = |n_0 = N \ n_1 = n_2 = \dots = 0\rangle \quad \text{i.e. } n_{\alpha} = N \delta_{\alpha 0} \quad ,$$

we get

$$\langle \Psi_0 | F | \Psi_0 \rangle = N f_{00} \quad , \tag{5.5.25}$$

$$\langle \Psi_0 | G | \Psi_0 \rangle = \frac{1}{2} N(N-1) g_{00,00} \quad . \tag{5.5.26}$$

In contrast, for fermions the uncorrelated ground state consists of a Slater determinant with the lowest N states occupied, while all higher lying single particle states are empty. Hence,

$$n_{\alpha} = \begin{cases} 1 & \text{for } 0 \leq \alpha \leq N \\ 0 & \text{for } N < \alpha \end{cases} \quad , \tag{5.5.27}$$

and the expectation values (5.5.22) and (5.5.23) turn into

$$\langle \Psi_0 | F | \Psi_0 \rangle = \sum_{\alpha=0}^{N-1} f_{\alpha\alpha} \quad , \quad (5.5.28)$$

$$\langle \Psi_0 | G | \Psi_0 \rangle = \frac{1}{2} \sum_{\alpha, \gamma=0}^{N-1} \left[g_{\alpha\gamma, \alpha\gamma} - g_{\alpha\gamma, \gamma\alpha} \right] \quad . \quad (5.5.29)$$

Once more we point to the case $\alpha = \gamma$, which is implicitly excluded, since it cancels out in the difference in square brackets in Eq. (5.5.29). We could thus include the corresponding matrix element $g_{\alpha\alpha, \alpha\alpha}$ in both the direct and the exchange term without changing the result.

5.6 Unitary transformations; field operators

Next we consider unitary transformations in Fock space as generated by an Hermitian single particle operator of the type (5.4.10) or (5.4.11). The transformation is thus mediated by the unitary operator

$$U = e^{-iF} \quad , \quad U^+ U = U U^+ = \mathcal{I} \quad . \quad (5.6.1)$$

From the Baker-Campbell-Hausdorff formula we have

$$\begin{aligned} \begin{Bmatrix} d_\gamma \\ c_\gamma \end{Bmatrix} &= U \begin{Bmatrix} b_\gamma \\ a_\gamma \end{Bmatrix} U^+ \\ &= \begin{Bmatrix} b_\gamma \\ a_\gamma \end{Bmatrix} - i [F, \begin{Bmatrix} b_\gamma \\ a_\gamma \end{Bmatrix}] + \frac{i^2}{2!} [F, [F, \begin{Bmatrix} b_\gamma \\ a_\gamma \end{Bmatrix}]] - \dots \quad . \end{aligned} \quad (5.6.2)$$

Turning to bosons first we calculate

$$[F, b_\gamma] = \sum_{\alpha\beta} \langle \chi_\alpha | f | \chi_\beta \rangle [b_\alpha^+ b_\beta, b_\gamma] \quad . \quad (5.6.3)$$

Using the commutator identity

$$[AB, C] = A \cdot [B, C] + [A, C] \cdot B \quad (5.6.4)$$

we obtain

$$\begin{aligned} [F, b_\gamma] &= \sum_{\alpha\beta} \langle \chi_\alpha | f | \chi_\beta \rangle \left\{ b_\alpha^+ \underbrace{[b_\beta, b_\gamma]}_0 + \underbrace{[b_\alpha^+, b_\gamma]}_{-\delta_{\alpha\gamma}} b_\beta \right\} \\ &= - \sum_{\beta} \langle \chi_\gamma | f | \chi_\beta \rangle b_\beta \quad . \end{aligned} \quad (5.6.5)$$

Using the identity

$$[AB, C] = A \cdot \{B, C\} + \{A, C\} \cdot B \quad (5.6.6)$$

the corresponding step yields for fermions

$$\begin{aligned} [F, a_\gamma] &= \sum_{\alpha\beta} \langle \chi_\alpha | f | \chi_\beta \rangle [a_\alpha^+ a_\beta, a_\gamma] \\ &= \sum_{\alpha\beta} \langle \chi_\alpha | f | \chi_\beta \rangle \left\{ a_\alpha^+ \underbrace{\{a_\beta, a_\gamma\}}_0 - \underbrace{\{a_\alpha^+, a_\gamma\}}_{\delta_{\alpha\gamma}} a_\beta \right\} \\ &= - \sum_{\beta} \langle \chi_\gamma | f | \chi_\beta \rangle a_\beta \quad . \end{aligned} \quad (5.6.7)$$

Hence, commutation with F results in a linear transformation of the annihilation operators. From the previous equations the higher commutators are easily calculated. We note

$$\begin{aligned} [F, [F, \begin{Bmatrix} b_\gamma \\ a_\gamma \end{Bmatrix}]] &= - \sum_{\beta} \langle \chi_\gamma | f | \chi_\beta \rangle [F, \begin{Bmatrix} b_\gamma \\ a_\gamma \end{Bmatrix}] \\ &= + \sum_{\beta\delta} \langle \chi_\gamma | f | \chi_\beta \rangle \langle \chi_\beta | f | \chi_\delta \rangle \begin{Bmatrix} b_\delta \\ a_\delta \end{Bmatrix} \\ &= + \sum_{\beta} \langle \chi_\gamma | f^2 | \chi_\beta \rangle \begin{Bmatrix} b_\beta \\ a_\beta \end{Bmatrix} \quad . \end{aligned} \quad (5.6.8)$$

Proceeding this way we finally arrive at the result

$$\begin{aligned} \begin{Bmatrix} d_\gamma \\ c_\gamma \end{Bmatrix} &= e^{-iF} \begin{Bmatrix} b_\gamma \\ a_\gamma \end{Bmatrix} e^{iF} \\ &= \sum_{\beta} \langle \chi_\gamma | \sum_{n=0}^{\infty} \frac{i^n}{n!} f^n | \chi_\beta \rangle \begin{Bmatrix} b_\beta \\ a_\beta \end{Bmatrix} \\ &= \sum_{\beta} \langle \chi_\gamma | e^{if} | \chi_\beta \rangle \begin{Bmatrix} b_\beta \\ a_\beta \end{Bmatrix} \\ &= \sum_{\beta} \langle \phi_\gamma | \chi_\beta \rangle \begin{Bmatrix} b_\beta \\ a_\beta \end{Bmatrix} \quad , \end{aligned} \quad (5.6.9)$$

where we have defined a set of transformed states by

$$|\phi_\gamma\rangle = e^{-if} |\chi_\gamma\rangle \quad . \quad (5.6.10)$$

For the adjoint operators, i.e. the creation operators we obtain from Eq. (5.6.9)

$$\begin{Bmatrix} d_\gamma^+ \\ c_\gamma^+ \end{Bmatrix} = e^{iF} \begin{Bmatrix} b_\gamma^+ \\ a_\gamma^+ \end{Bmatrix} e^{-iF}$$

$$= \sum_{\beta} \left\{ \begin{array}{c} b_{\beta}^{+} \\ a_{\beta}^{+} \end{array} \right\} \langle \chi_{\beta} | \phi_{\gamma} \rangle \quad . \quad (5.6.11)$$

To summarize, both Eqs. (5.6.9) and (5.6.11) mediate a unitary transformation from the orthonormal basis spanned by functions $|\chi_{\beta}\rangle$ to a likewise orthonormal basis made of function $|\phi_{\gamma}\rangle$ and the operators c_{γ} , c_{γ}^{+} , d_{γ} , and d_{γ}^{+} are the annihilation and creation operators corresponding to the new basis set. This is seen from the identities

$$\left\{ \begin{array}{c} d_{\gamma}^{+} \\ c_{\gamma}^{+} \end{array} \right\} |0\rangle = \sum_{\beta} \left\{ \begin{array}{c} b_{\beta}^{+} \\ a_{\beta}^{+} \end{array} \right\} |0\rangle \langle \chi_{\beta} | \phi_{\gamma} \rangle = \sum_{\beta} |\chi_{\beta}\rangle \langle \chi_{\beta} | \phi_{\gamma} \rangle = |\phi_{\gamma}\rangle \quad . \quad (5.6.12)$$

We furthermore conclude that the Hermitian single particle operators F in Fock space generate unitary transformations of the single particle basis, $U = e^{-iF}$.

A very important application of Eqs. (5.6.9) and (5.6.11) results from choosing the single particle wave functions $|\phi_{\gamma}\rangle$ as the eigenstates $|\mathbf{x}\rangle$ of the particle position operator. For particles with spin we would opt for states $|\mathbf{x}, m_s\rangle$, with $m_s = -s, \dots, +s$, which are thus δ -functions in space and Kronecker δ 's with respect to the spin. We note

$$\langle \mathbf{x}, m_s | \chi_{\alpha} \rangle = \sum_{m'_s} \int d^3 \mathbf{x}' \chi_{\alpha; m'_s}(\mathbf{x}') \delta(\mathbf{x} - \mathbf{x}') \delta_{m_s m'_s} = \chi_{\alpha; m_s}(\mathbf{x}) \quad , \quad (5.6.13)$$

where the first index α includes *all* quantum numbers characterizing the states χ_{α} and the second index m'_s denotes the projection of these states onto the corresponding spin channel. In choosing this notation we take implicitly care of the situation that the states χ_{α} might be linear combinations of functions with different m'_s values, hence, might be mixed spin states. Obviously, the eigenfunctions $|\mathbf{x}, m_s\rangle$ are orthogonal to each other and they span the single particle Hilbert space according to

$$\langle \mathbf{x}, m_s | \mathbf{x}', m'_s \rangle = \delta(\mathbf{x} - \mathbf{x}') \delta_{m_s m'_s} \quad (5.6.14)$$

$$\sum_{m_s} \int d^3 \mathbf{x} |\mathbf{x}, m_s\rangle \langle \mathbf{x}, m_s| = \mathcal{I} \quad . \quad (5.6.15)$$

Furthermore, they allow to define creation and annihilation operators by

$$\psi^{+}(\mathbf{x}, m_s) = \sum_{\beta} \left\{ \begin{array}{c} b_{\beta}^{+} \quad (\text{bosons}) \\ a_{\beta}^{+} \quad (\text{fermions}) \end{array} \right\} \langle \chi_{\beta} | \mathbf{x}, m_s \rangle \quad , \quad (5.6.16)$$

$$\psi(\mathbf{x}, m_s) = \sum_{\beta} \langle \mathbf{x}, m_s | \chi_{\beta} \rangle \left\{ \begin{array}{c} b_{\beta} \quad (\text{bosons}) \\ a_{\beta} \quad (\text{fermions}) \end{array} \right\} \quad , \quad (5.6.17)$$

which are the so-called field operators at position \mathbf{x} with spin m_s . Since the unitary transformation conserves the commutation relations the corresponding

expressions for the field operators are immediately written down as

$$[\psi(\mathbf{x}', m'_s), \psi^+(\mathbf{x}, m_s)] = \delta^3(\mathbf{x}' - \mathbf{x}) \delta_{m'_s, m_s} \cdot \mathcal{I} \quad \text{for bosons} \quad , \quad (5.6.18)$$

$$\{\psi(\mathbf{x}', m'_s), \psi^+(\mathbf{x}, m_s)\} = \delta^3(\mathbf{x}' - \mathbf{x}) \delta_{m'_s, m_s} \cdot \mathcal{I} \quad \text{for fermions} \quad , \quad (5.6.19)$$

while all other commutators and anticommutators vanish. Furthermore, in close analogy to the definition of the occupation number operators (5.3.7) and (5.3.17) we construct the operator of the particle density,

$$\hat{\rho}(\mathbf{x}) = \psi^+(\mathbf{x})\psi(\mathbf{x}) = \sum_s \psi^+(\mathbf{x}, m_s)\psi(\mathbf{x}, m_s) \quad , \quad (5.6.20)$$

and the operator of the total particle number,

$$\hat{N} = \int d^3\mathbf{x} \hat{\rho}(\mathbf{x}) = \int d^3\mathbf{x} \psi^+(\mathbf{x})\psi(\mathbf{x}) \quad . \quad (5.6.21)$$

From Eq. (5.6.20) we may moreover derive the operators of the mass and charge density as

$$\hat{\rho}_m(\mathbf{x}) = m \psi^+(\mathbf{x})\psi(\mathbf{x}) \quad , \quad (5.6.22)$$

$$\hat{\rho}_q(\mathbf{x}) = q \psi^+(\mathbf{x})\psi(\mathbf{x}) \quad . \quad (5.6.23)$$

Finally, we return to the Hamiltonian (4.1.6) describing the many-body states of the electrons subject to both the ion-electron and the electron-electron interaction. In order to derive its representation in terms of field operators we start from the intermediate expressions (5.4.13) and (5.4.24) specifying the one and two particle terms. Ignoring, for the time being, the spin degrees of freedom and assuming local potentials throughout we calculate the matrix elements as

$$\begin{aligned} \langle \mathbf{r}'_1 | v_{ext}(\mathbf{r}) | \mathbf{r}_1 \rangle &= \int d^3\mathbf{r} v_{ext}(\mathbf{r}) \delta^3(\mathbf{r}'_1 - \mathbf{r}_1) \delta^3(\mathbf{r}_1 - \mathbf{r}) \\ &= \delta^3(\mathbf{r}'_1 - \mathbf{r}_1) v_{ext}(\mathbf{r}_1) \quad , \end{aligned} \quad (5.6.24)$$

$$\begin{aligned} \{ \langle \mathbf{r}'_1 | \otimes \langle \mathbf{r}'_2 | \} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \{ | \mathbf{r}_1 \rangle \otimes | \mathbf{r}_2 \rangle \} \\ = \delta^3(\mathbf{r}'_1 - \mathbf{r}_1) \delta^3(\mathbf{r}'_2 - \mathbf{r}_2) \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad . \end{aligned} \quad (5.6.25)$$

We thus arrive at the following expression for the Hamiltonian

$$\begin{aligned} H_0 &= \int d^3\mathbf{r} \psi^+(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} \psi(\mathbf{r}) \\ &\quad + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi^+(\mathbf{r})\psi^+(\mathbf{r}') \times \psi(\mathbf{r}')\psi(\mathbf{r}) \end{aligned}$$

$$\begin{aligned}
&= \int d^3\mathbf{r} \left\{ \frac{\hbar^2}{2m} [\nabla\psi^+(\mathbf{r})] \cdot [\nabla\psi(\mathbf{r})] + v_{ext}(\mathbf{r})\hat{\rho}(\mathbf{r}) \right\} \\
&\quad + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \psi^+(\mathbf{r})\psi^+(\mathbf{r}') \times \psi(\mathbf{r}')\psi(\mathbf{r}) \quad , \\
\end{aligned} \tag{5.6.26}$$

where we used an integration by parts for the kinetic energy term as well as Eq. (5.6.20) for the particle density. Note that Eq. (5.6.26) is just a particular representation of the more general result (5.4.26).

In passing we mention that the form (5.6.26) of the Hamiltonian, besides being a particular description of the interacting electron system, suggests an alternative interpretation of Eq. (5.6.26) as the energy integral of a classical field theory, where the field operators are spatial functions with $\psi^+\psi = |\psi|^2$ rather than operators and $\psi(\mathbf{r})$ plays the role of a $(2s + 1)$ -component field amplitude. As a consequence, the whole formalism derived in this chapter may be obtained by formally assigning a classical field theory with field amplitude $\psi(\mathbf{r})$ and the energy integral (5.6.26) to the system of identical particles and only after this interpreting ψ, ψ^* as adjoint operators ψ, ψ^+ with commutation relations (5.6.18) and anticommutation relations (5.6.19) for $2s + 1$ even and odd, respectively. The Fock space description presented in this chapter is thus equivalent to the quantization of a classical field theory. This observation is of particular value for systems, which classically are described by a field theory as e.g. the electromagnetic field.

5.7 Electron density operators

In this section we apply the notions learned in the previous sections to the particular case of the real space representation of the electronic system. Hence, we are dealing with spin- $\frac{1}{2}$ particles, $s = \frac{1}{2}$, $m_s = \pm\frac{1}{2} =: \sigma$ and Eqs. (5.6.13) to (5.6.15) read as

$$\langle \mathbf{x}, \sigma | \mathbf{x}', \sigma' \rangle = \delta(\mathbf{x} - \mathbf{x}') \delta_{\sigma\sigma'} \tag{5.7.1}$$

$$\sum_{\sigma} \int d^3\mathbf{x} |\mathbf{x}, \sigma\rangle \langle \mathbf{x}, \sigma| = \mathcal{I} \quad . \tag{5.7.2}$$

$$\langle \mathbf{x}, \sigma | \chi_{\alpha} \rangle = \chi_{\alpha;\sigma}(\mathbf{x}) \quad , \tag{5.7.3}$$

where the index α covers all quantum numbers characterizing the states χ_{α} and the second index denotes the projection onto spin channel σ ; note that χ_{α} might be in a mixed spin state. According to Eqs. (5.6.16) and (5.6.17) the field operators then assume the form

$$\psi_{\sigma}^+(\mathbf{x}) = \sum_{\alpha} a_{\alpha}^+ \langle \chi_{\alpha} | \mathbf{x}, \sigma \rangle = \sum_{\alpha} \chi_{\alpha;\sigma}^*(\mathbf{x}) a_{\alpha}^+ \quad , \tag{5.7.4}$$

$$\psi_{\sigma}(\mathbf{x}) = \sum_{\alpha} a_{\alpha} \langle \mathbf{x}, \sigma | \chi_{\alpha} \rangle = \sum_{\alpha} \chi_{\alpha;\sigma}(\mathbf{x}) a_{\alpha} \quad , \tag{5.7.5}$$

and fulfil the anticommutation relations (5.6.19). Combining Eqs. (5.7.4) and (5.7.5) we arrive at the definition of the spin-dependent electron density operator

$$\hat{\rho}_\sigma(\mathbf{x}) = \psi_\sigma^\dagger(\mathbf{x})\psi_\sigma(\mathbf{x}) = \sum_{\alpha\beta} \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\beta;\sigma}(\mathbf{x})a_\alpha^\dagger a_\beta \quad , \quad (5.7.6)$$

which gives rise to the definition of the electron density and spin density operators,

$$\hat{\rho}(\mathbf{x}) = \sum_{\sigma} \hat{\rho}_\sigma(\mathbf{x}) \quad , \quad (5.7.7)$$

$$\hat{m}_z(\mathbf{x}) = \sum_{\sigma} z_\sigma \hat{\rho}_\sigma(\mathbf{x}) \quad , \quad (5.7.8)$$

where

$$z_\sigma = \begin{cases} +1 & \text{for } \sigma = +\frac{1}{2} \\ -1 & \text{for } \sigma = -\frac{1}{2} \end{cases} \quad . \quad (5.7.9)$$

Mass and charge density operators may be easily constructed in analogy to Eqs. (5.6.22) and (5.6.23) by multiplying the density operator with the electron mass and charge, respectively, and, finally, we get for the operator of the total electron number by integrating the density operator over all space,

$$\hat{N} = \int d^3x \hat{\rho}(\mathbf{x}) \quad . \quad (5.7.10)$$

We complement the definition (5.7.6) of the electron density operator with an alternative form,

$$\hat{\rho}_\sigma(\mathbf{x}) = \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i) \delta_{\sigma\sigma_i} \quad , \quad (5.7.11)$$

where the sum over i includes all electrons. Obviously, the electron density operator is a single-particle operator of the general form (5.4.1) with $f^{(i)} = \delta(\mathbf{x} - \mathbf{x}_i) \delta_{\sigma\sigma_i}$ and matrix elements

$$f_{\alpha\beta} = \langle \chi_\alpha^{(i)} | \delta(\mathbf{x} - \mathbf{x}_i) \delta_{\sigma\sigma_i} | \chi_\beta^{(i)} \rangle = \chi_{\alpha;\sigma}^*(\mathbf{x}) \chi_{\beta;\sigma}(\mathbf{x}) \quad . \quad (5.7.12)$$

As a consequence, transferring the density operator to the language of second quantization we obtain according to Eq. (5.4.11)

$$\hat{\rho}_\sigma(\mathbf{x}) = \sum_{\alpha\beta} \chi_{\alpha;\sigma}^*(\mathbf{x}) \chi_{\beta;\sigma}(\mathbf{x}) a_\alpha^\dagger a_\beta \quad , \quad (5.7.13)$$

which is, of course, identical to Eq. (5.7.6). From the latter identity the electron density is easily calculated as the expectation value of the electron density operator,

$$\rho_\sigma(\mathbf{x}) = \langle \Psi_0 | \hat{\rho}_\sigma(\mathbf{x}) | \Psi_0 \rangle$$

$$\begin{aligned}
&= \sum_{\alpha\beta} \underbrace{\chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\beta;\sigma}(\mathbf{x})}_{f_{\alpha\beta}} \langle \Psi_0 | a_{\alpha}^{\dagger} a_{\beta} | \Psi_0 \rangle \\
&= \sum_{\alpha} \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\alpha;\sigma}(\mathbf{x}) \rho_1^{(0)}(\alpha; \alpha) \\
&= \sum_{\alpha} \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\alpha;\sigma}(\mathbf{x}) n_{\alpha} \\
&= \sum_{\alpha}^{\text{occ}} |\chi_{\alpha;\sigma}(\mathbf{x})|^2 \quad , \quad (5.7.14)
\end{aligned}$$

i.e. the electron density arises as the square of the single-particle wave functions, summed over all occupied states.

For the following chapters it will be useful to have an extension of the density operator at hand,

$$\hat{\rho}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = \psi_{\sigma'}^{\dagger}(\mathbf{x}')\psi_{\sigma}(\mathbf{x}) \quad . \quad (5.7.15)$$

Using the definitions (5.7.4) and (5.7.5) of the field operators we thus obtain

$$\hat{\rho}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = \sum_{\alpha\beta} \chi_{\alpha;\sigma'}^*(\mathbf{x}')\chi_{\beta;\sigma}(\mathbf{x}) a_{\alpha}^{\dagger} a_{\beta} \quad , \quad (5.7.16)$$

and, with the help of Eq. (5.5.5), we get for the ground state expectation value the result

$$\begin{aligned}
\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') &= \langle \Psi_0 | \hat{\rho}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') | \Psi_0 \rangle \\
&= \sum_{\alpha\beta} \underbrace{\chi_{\alpha;\sigma'}^*(\mathbf{x}')\chi_{\beta;\sigma}(\mathbf{x})}_{f_{\alpha\beta}} \langle \Psi_0 | a_{\alpha}^{\dagger} a_{\beta} | \Psi_0 \rangle \\
&= \sum_{\alpha} \chi_{\alpha;\sigma'}^*(\mathbf{x}')\chi_{\alpha;\sigma}(\mathbf{x}) \rho_1^{(0)}(\alpha; \alpha) \\
&= \sum_{\alpha}^{\text{occ}} \chi_{\alpha;\sigma'}^*(\mathbf{x}')\chi_{\alpha;\sigma}(\mathbf{x}) \\
&= (\rho_{\sigma'\sigma}(\mathbf{x}'; \mathbf{x}))^* \quad , \quad (5.7.17)
\end{aligned}$$

where in the second but last line the summation includes only the occupied states. The quantity $\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')$ is called the spin-dependent density matrix, which for $\mathbf{x} = \mathbf{x}'$ reduces to the spin density matrix at position \mathbf{x} and for $\sigma = \sigma'$ to the density matrix. In order to simplify writing we thus define

$$\rho_{\sigma\sigma'}(\mathbf{x}) = \rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x})\delta(\mathbf{x} - \mathbf{x}') \quad , \quad (5.7.18)$$

$$\rho_{\sigma}(\mathbf{x}) = \rho_{\sigma\sigma}(\mathbf{x})\delta_{\sigma\sigma'} \quad . \quad (5.7.19)$$

A particular appealing representation arises from the second but last line of Eq. (5.7.17), where the density matrix is given by the sum over the occupied single particle orbitals. We will use this form later on in the discussion of the

homogeneous electron gas.

Next we turn to a different extension of the density operator (5.7.6), namely the product of two such operators, in order to measure the probability of finding an electron with spin σ at position \mathbf{x} and a second electron with spin σ' at position \mathbf{x}' . However, in doing so we want to exclude the case where both electrons are identical and thus, starting from the alternative definition (5.7.11) of the electron density operator, define rather than the simple product of the corresponding density operators the quantity

$$\begin{aligned}
\hat{P}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') &= \hat{P}_{\sigma'\sigma}(\mathbf{x}'; \mathbf{x}) \\
&= \sum_{\substack{i,j \\ j \neq i}}^N \delta(\mathbf{x} - \mathbf{x}_i) \delta_{\sigma\sigma_i} \delta(\mathbf{x}' - \mathbf{x}_j) \delta_{\sigma'\sigma_j} \\
&= \sum_{i,j}^N (1 - \delta_{ij}) \delta(\mathbf{x} - \mathbf{x}_i) \delta_{\sigma\sigma_i} \delta(\mathbf{x}' - \mathbf{x}_j) \delta_{\sigma'\sigma_j} \\
&= \sum_{i,j}^N \delta(\mathbf{x} - \mathbf{x}_i) \delta_{\sigma\sigma_i} \delta(\mathbf{x}' - \mathbf{x}_j) \delta_{\sigma'\sigma_j} - \delta(\mathbf{x}' - \mathbf{x}) \delta_{\sigma'\sigma} \sum_i^N \delta(\mathbf{x} - \mathbf{x}_i) \delta_{\sigma\sigma_i} \\
&= \hat{\rho}_\sigma(\mathbf{x}) \hat{\rho}_{\sigma'}(\mathbf{x}') - \delta(\mathbf{x}' - \mathbf{x}) \delta_{\sigma'\sigma} \hat{\rho}_\sigma(\mathbf{x}) \quad . \quad (5.7.20)
\end{aligned}$$

Hence, in order to avoid the “self-interaction” we have to subtract the single density operator from the simple product. As for the density operator above, we recognize that the operator (5.7.20) has the form of the general two-particle operator (5.4.15) for an N -particle system with

$$g^{(i,j)} = 2 \cdot \delta(\mathbf{x} - \mathbf{x}_i) \delta_{\sigma\sigma_i} \delta(\mathbf{x}' - \mathbf{x}_j) \delta_{\sigma'\sigma_j}$$

and matrix elements, which, according to Eq. (5.4.16) read as

$$\begin{aligned}
g_{\alpha\gamma,\beta\delta} &= \left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} g^{(1,2)} \left\{ | \chi_\beta^{(1)} \rangle \otimes | \chi_\delta^{(2)} \rangle \right\} \\
&= \left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} 2 \cdot \delta(\mathbf{x} - \mathbf{x}_1) \delta_{\sigma\sigma_1} \delta(\mathbf{x}' - \mathbf{x}_2) \delta_{\sigma'\sigma_2} \left\{ | \chi_\beta^{(1)} \rangle \otimes | \chi_\delta^{(2)} \rangle \right\} \\
&= \chi_{\alpha;\sigma}^*(\mathbf{x}) \chi_{\gamma;\sigma'}^*(\mathbf{x}') \chi_{\beta;\sigma}(\mathbf{x}) \chi_{\delta;\sigma'}(\mathbf{x}') \quad . \quad (5.7.21)
\end{aligned}$$

Following Eq. (5.4.23) we thus arrive at the Fock-space representation

$$\begin{aligned}
\hat{P}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') &= \hat{\rho}_\sigma(\mathbf{x}) \hat{\rho}_{\sigma'}(\mathbf{x}') - \delta(\mathbf{x}' - \mathbf{x}) \delta_{\sigma'\sigma} \hat{\rho}_\sigma(\mathbf{x}) \\
&= \sum_{\alpha\gamma} \sum_{\beta\delta} \chi_{\alpha;\sigma}^*(\mathbf{x}) \chi_{\gamma;\sigma'}^*(\mathbf{x}') \chi_{\beta;\sigma}(\mathbf{x}) \chi_{\delta;\sigma'}(\mathbf{x}') a_\alpha^+ a_\gamma^+ a_\delta a_\beta \quad , \quad (5.7.22)
\end{aligned}$$

and, comparing to Eq. (5.5.29), we obtain for the ground state expectation value the result

$$P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = \langle \Psi_0 | \hat{P}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') | \Psi_0 \rangle$$

$$\begin{aligned}
&= \sum_{\alpha\gamma}^{occ} \left[\chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\gamma;\sigma'}^*(\mathbf{x}')\chi_{\alpha;\sigma}(\mathbf{x})\chi_{\gamma;\sigma'}(\mathbf{x}') \right. \\
&\quad \left. - \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\gamma;\sigma'}^*(\mathbf{x}')\chi_{\gamma;\sigma}(\mathbf{x})\chi_{\alpha;\sigma'}(\mathbf{x}') \right] \\
&= \rho_{\sigma}(\mathbf{x}) \cdot \rho_{\sigma'}(\mathbf{x}') - \rho_{\sigma'\sigma}(\mathbf{x}'; \mathbf{x})\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') \\
&= \rho_{\sigma}(\mathbf{x}) \cdot \rho_{\sigma'}(\mathbf{x}') - |\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')|^2 \quad , \quad (5.7.23)
\end{aligned}$$

where we have used the results (5.7.17) to (5.7.19) for the density as well as the density matrix.

In passing we write down an alternative representation of the operator $\hat{P}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')$ in terms of field operators as

$$\hat{P}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = \psi_{\sigma}^{\dagger}(\mathbf{x})\psi_{\sigma'}^{\dagger}(\mathbf{x}')\psi_{\sigma'}(\mathbf{x}')\psi_{\sigma}(\mathbf{x}) \quad . \quad (5.7.24)$$

Using the anticommutation relations (5.6.19) we readily transfer the previous expression into the form

$$\begin{aligned}
\hat{P}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') &= -\psi_{\sigma}^{\dagger}(\mathbf{x})\psi_{\sigma'}^{\dagger}(\mathbf{x}')\psi_{\sigma}(\mathbf{x})\psi_{\sigma'}(\mathbf{x}') \\
&= \psi_{\sigma}^{\dagger}(\mathbf{x})\psi_{\sigma}(\mathbf{x})\psi_{\sigma'}^{\dagger}(\mathbf{x}')\psi_{\sigma'}(\mathbf{x}') - \delta(\mathbf{x}' - \mathbf{x})\delta_{\sigma'\sigma}\psi_{\sigma}^{\dagger}(\mathbf{x})\psi_{\sigma'}(\mathbf{x}') \\
&= \hat{\rho}_{\sigma}(\mathbf{x})\hat{\rho}_{\sigma'}(\mathbf{x}') - \delta(\mathbf{x}' - \mathbf{x})\delta_{\sigma'\sigma}\hat{\rho}_{\sigma}(\mathbf{x}) \quad , \quad (5.7.25)
\end{aligned}$$

which, hence, is identical to the definition (5.7.20). Finally, combining Eqs. (5.7.23) and (5.7.24) we obtain the result

$$P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = \langle \Psi_0 | \psi_{\sigma}^{\dagger}(\mathbf{x})\psi_{\sigma'}^{\dagger}(\mathbf{x}')\psi_{\sigma'}(\mathbf{x}')\psi_{\sigma}(\mathbf{x}) | \Psi_0 \rangle \quad , \quad (5.7.26)$$

which will be useful lateron.

Again it is useful to define a non-diagonal generalization of the operator $\hat{P}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')$ as

$$\begin{aligned}
&\hat{P}_{\sigma'''\sigma'\sigma\sigma''}(\mathbf{x}'''\mathbf{x}'; \mathbf{x}\mathbf{x}'') \\
&= \hat{\rho}_{\sigma'''\sigma''}(\mathbf{x}'''; \mathbf{x}'')\hat{\rho}_{\sigma'\sigma}(\mathbf{x}'; \mathbf{x}) - \delta(\mathbf{x} - \mathbf{x}''')\delta_{\sigma\sigma'''}\hat{\rho}_{\sigma'\sigma''}(\mathbf{x}'; \mathbf{x}'') \\
&= \psi_{\sigma''}^{\dagger}(\mathbf{x}'')\psi_{\sigma'''}^{\dagger}(\mathbf{x}''')\psi_{\sigma}^{\dagger}(\mathbf{x})\psi_{\sigma'}(\mathbf{x}') \\
&\quad - \delta(\mathbf{x} - \mathbf{x}''')\delta_{\sigma\sigma'''}\psi_{\sigma''}^{\dagger}(\mathbf{x}'')\psi_{\sigma'}(\mathbf{x}') \quad . \quad (5.7.27)
\end{aligned}$$

The last line can be further evaluated using the anticommutation relations (5.6.19) of the field operators, which, however, have the same algebra as the creation and annihilation operators (5.3.14) and (5.3.15). The latter fulfil the equivalent anticommutation relations (5.3.33) and we may thus directly adopt the identity (5.4.21) for the field operators. Hence, we get the following expression

$$\hat{P}_{\sigma'''\sigma'\sigma\sigma''}(\mathbf{x}'''\mathbf{x}'; \mathbf{x}\mathbf{x}'') = \psi_{\sigma}^{\dagger}(\mathbf{x})\psi_{\sigma''}^{\dagger}(\mathbf{x}'')\psi_{\sigma'''}(\mathbf{x}''')\psi_{\sigma'}(\mathbf{x}') \quad . \quad (5.7.28)$$

Inserting into this the definitions (5.7.4) and (5.7.5) of the field operators we obtain

$$\begin{aligned} & \hat{P}_{\sigma'''\sigma'\sigma\sigma''}(\mathbf{x}'''\mathbf{x}';\mathbf{x}\mathbf{x}'') \\ &= \sum_{\alpha\gamma} \sum_{\beta\delta} \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\gamma;\sigma''}^*(\mathbf{x}'')\chi_{\beta;\sigma'}(\mathbf{x}')\chi_{\delta;\sigma'''}(\mathbf{x}''')a_{\alpha}^{\dagger}a_{\gamma}^{\dagger}a_{\delta}a_{\beta} \quad , \quad (5.7.29) \end{aligned}$$

which, for $\mathbf{x} = \mathbf{x}'$, $\sigma = \sigma'$ and $\mathbf{x}'' = \mathbf{x}'''$, $\sigma'' = \sigma'''$ reduces to Eq. (5.7.22). In close analogy to Eq. (5.7.23) the ground state expectation value is now calculated as

$$\begin{aligned} & P_{\sigma'''\sigma'\sigma\sigma''}(\mathbf{x}'''\mathbf{x}';\mathbf{x}\mathbf{x}'') \\ &= \langle \Psi_0 | \hat{P}_{\sigma\sigma''\sigma'''\sigma'}(\mathbf{x}\mathbf{x}'';\mathbf{x}'''\mathbf{x}') | \Psi_0 \rangle \\ &= \sum_{\alpha\gamma} \sum_{\beta\delta} \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\gamma;\sigma''}^*(\mathbf{x}'')\chi_{\beta;\sigma'}(\mathbf{x}')\chi_{\delta;\sigma'''}(\mathbf{x}''') \langle \Psi_0 | a_{\alpha}^{\dagger}a_{\gamma}^{\dagger}a_{\delta}a_{\beta} | \Psi_0 \rangle \\ &= \sum_{\alpha\gamma} \sum_{\beta\delta} \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\gamma;\sigma''}^*(\mathbf{x}'')\chi_{\beta;\sigma'}(\mathbf{x}')\chi_{\delta;\sigma'''}(\mathbf{x}''') \rho_2^{(0)}(\beta\delta;\alpha\gamma) \\ &= \sum_{\alpha\gamma} \sum_{\beta\delta} \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\gamma;\sigma''}^*(\mathbf{x}'')\chi_{\beta;\sigma'}(\mathbf{x}')\chi_{\delta;\sigma'''}(\mathbf{x}''') \\ & \quad \left[\rho_1^{(0)}(\beta;\alpha) \cdot \rho_1^{(0)}(\delta;\gamma) - \rho_1^{(0)}(\beta;\gamma) \cdot \rho_1^{(0)}(\delta;\alpha) \right] \\ &= \sum_{\alpha\gamma}^{occ} \left[\chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\gamma;\sigma''}^*(\mathbf{x}'')\chi_{\alpha;\sigma'}(\mathbf{x}')\chi_{\gamma;\sigma'''}(\mathbf{x}''') \right. \\ & \quad \left. - \chi_{\alpha;\sigma}^*(\mathbf{x})\chi_{\gamma;\sigma''}^*(\mathbf{x}'')\chi_{\gamma;\sigma'}(\mathbf{x}')\chi_{\alpha;\sigma'''}(\mathbf{x}''') \right] \\ &= \rho_{\sigma'\sigma}(\mathbf{x}';\mathbf{x})\rho_{\sigma'''\sigma''}(\mathbf{x}''';\mathbf{x}'') - \rho_{\sigma'''\sigma}(\mathbf{x}''';\mathbf{x})\rho_{\sigma'\sigma''}(\mathbf{x}';\mathbf{x}'') \quad , \quad (5.7.30) \end{aligned}$$

where we have used the definition (5.5.6) as well as the identities (5.5.11), (5.5.19), and (5.7.17). The summation in the last two lines of Eq. (5.7.30) includes only the occupied single particle states. Again, with the help of Eq. (5.7.18), we come back to the result (5.7.23) for $\mathbf{x} = \mathbf{x}'$, $\sigma = \sigma'$ and $\mathbf{x}'' = \mathbf{x}'''$, $\sigma'' = \sigma'''$.

Investigating the latter, diagonal case in a bit more detail we realize that, in the same manner as the reduced density matrix (5.5.29), the probability of finding an electron with spin σ at position \mathbf{x} and a second electron with spin σ' at position \mathbf{x}' is not just a simple product of the densities but is made of a direct and an exchange term. Note that the self-interaction ($\alpha = \beta = \gamma = \delta$) is cancelled automatically in the difference of these two terms. While the direct term is mainly the product of the densities the exchange term results from the non-classical identity of particles and causes a contribution, which in the language of probability theory is named correlation. Nevertheless, within many-body theory one distinguishes two different origins of correlation, namely that due to the identity of particles and that arising from the interaction of

the particles. While the first is usually called exchange the name correlation is reserved for the latter contribution.

We close this section by defining two types of correlation (in the broader sense of the word) functions, namely the pair-distribution or pair-correlation function

$$g_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = \frac{P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')}{\rho_{\sigma}(\mathbf{x}) \cdot \rho_{\sigma'}(\mathbf{x}')} \quad (5.7.31)$$

as well as the function

$$h_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') - \rho_{\sigma}(\mathbf{x}) \cdot \rho_{\sigma'}(\mathbf{x}') \quad , \quad (5.7.32)$$

where the symbols g and h were chosen along convention. The function g is usually designated as the pair-distribution or pair-correlation function. Combining these definitions with Eq. (5.7.23) we finally note

$$g_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = 1 - \frac{|\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')|^2}{\rho_{\sigma}(\mathbf{x}) \cdot \rho_{\sigma'}(\mathbf{x}')} \quad , \quad (5.7.33)$$

$$h_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = -|\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')|^2 \quad . \quad (5.7.34)$$

Chapter 6

Hartree-Fock theory

6.1 The Hartree-Fock equations

Having learnt about the particularities of systems of identical particles as well as about the efficient formulation provided by the occupation number representation of many-body states we are now in a position to combine these new means with the variational determination of the electronic wave function. In section 4.4 the latter procedure led to the Hartree equations, which, however, included the many-body wave functions as direct products of single particle functions. Following the work by Fock and Slater [54, 149] we will in the present section combine the variational method with the correctly antisymmetrized many-body wave function in order to arrive at a better prescription of the electronic ground state.

To be concrete, we replace Eq. (4.4.1) by a Slater determinant, Eq. (5.2.4),

$$|\psi_{-}\rangle = (N!)^{-\frac{1}{2}} \sum_{P \in S_N} (-)^P \mathcal{P}_P \bigotimes_i^N |\chi_{\alpha_i}^{(i)}\rangle \quad , \quad (6.1.1)$$

where we still assume the single particle orbitals to be normalized according to Eq. (5.2.15). Again, we consider the Hamiltonian (4.1.6) and calculate the energy functional, now with the Slater determinants (6.1.1),

$$\langle H_0 \rangle_{\psi} = \langle \psi_{-} | H_0 | \psi_{-} \rangle = \langle \psi_{-} | H_0^{\{1\}} | \psi_{-} \rangle + \langle \psi_{-} | H_0^{\{2\}} | \psi_{-} \rangle \quad . \quad (6.1.2)$$

Note that the correct normalization of the many-body wave function (6.1.1) is implied by the normalization of the single particle orbitals, Eq. (5.2.15). Moreover, note that, in contrast to Eq. (4.4.3), we have not yet fixed a particular representation of the wave function.

In order to evaluate the functional (6.1.2) we fall back on the results of section 5.5, where we expressed the functionals of one- and two-particle operators in terms of the corresponding reduced density matrices. We recall, in particular, Eqs. (5.5.28) and (5.5.29) with the matrix elements on the right hand

side given by Eqs. (5.4.2) and (5.4.16). Since the Hamiltonian (4.1.6) is built from one- and two-particle operators we may read off the corresponding matrix elements from a comparison of its occupation number representation, Eq. (5.4.26), to the general identities (5.4.11) and (5.4.23). Inserting these matrix elements into Eqs. (5.5.28) and (5.5.29) we obtain

$$\begin{aligned}
\langle H_0 \rangle_\psi &= \sum_\alpha \langle \chi_\alpha | \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} | \chi_\alpha \rangle \\
&+ \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{\alpha\gamma \\ \alpha \neq \gamma}} \left[\left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left\{ | \chi_\alpha^{(1)} \rangle \otimes | \chi_\gamma^{(2)} \rangle \right\} \right. \\
&\quad \left. - \left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left\{ | \chi_\gamma^{(1)} \rangle \otimes | \chi_\alpha^{(2)} \rangle \right\} \right] , \tag{6.1.3}
\end{aligned}$$

where we identify the direct and exchange contributions to the two-particle term as in the context of Eq. (5.5.29). In Eq. (6.1.3) we have explicitly excluded the term $\alpha = \gamma$. Yet, as was already discussed at the end of Sec. 5.5, this exclusion is implicit in the difference in the square brackets in Eq. (6.1.3), since both terms are identical for $\alpha = \gamma$. Nevertheless, care has to be taken, when the direct and exchange term are treated in a different manner and the exact cancellation of the self-interaction matrix elements is violated. This happens to be the case in the local density approximation, where it is the source of serious errors, which urgently call for corrections. In order to be aware of the self-interaction terms we will thus keep the extra exclusion of the terms $\alpha = \gamma$ in our notation.

In the next step we transform the previous intermediate result to the real space representation. In doing so we fall back on the prescription presented in Sec. 5.7 and use the eigenstates $|\mathbf{x}, \sigma\rangle$ of the electron position/spin operator, for which we noted the basic identities in Eqs. (5.7.1) to (5.7.3). Inserting now Eq. (5.7.2) into Eq. (6.1.3) and using the identity (5.7.3) we get for the one-particle part of the energy functional

$$\begin{aligned}
\langle H_0^{\{1\}} \rangle_\psi &= \sum_\alpha \sum_{\sigma\sigma'} \int d^3\mathbf{x} \int d^3\mathbf{x}' \langle \chi_\alpha | \mathbf{x}, \sigma \rangle \\
&\quad \langle \mathbf{x}, \sigma | \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} | \mathbf{x}', \sigma' \rangle \langle \mathbf{x}', \sigma' | \chi_\alpha \rangle \\
&= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} \chi_{\alpha;\sigma}(\mathbf{r}) . \tag{6.1.4}
\end{aligned}$$

In the last step we have used, in addition, Eq. (5.6.24). The two particle terms entering Eq. (6.1.3) are treated in complete analogy. Using Eq. (5.6.25) we

write for the direct term

$$\begin{aligned}
& \left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left\{ | \chi_\alpha^{(1)} \rangle \otimes | \chi_\gamma^{(2)} \rangle \right\} \\
&= \sum_{\sigma\sigma'} \sum_{\sigma''\sigma'''} \int d^3\mathbf{x} \int d^3\mathbf{x}' \int d^3\mathbf{x}'' \int d^3\mathbf{x}''' \langle \chi_\alpha^{(1)} | \mathbf{x}, \sigma \rangle \langle \chi_\gamma^{(2)} | \mathbf{x}', \sigma' \rangle \\
&\quad \{ \langle \mathbf{x}, \sigma | \otimes \langle \mathbf{x}', \sigma' | \} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \{ | \mathbf{x}'', \sigma'' \rangle \otimes | \mathbf{x}''', \sigma''' \rangle \} \\
&\quad \langle \mathbf{x}'', \sigma'' | \chi_\alpha^{\{1\}} \rangle \langle \mathbf{x}''', \sigma''' | \chi_\gamma^{\{2\}} \rangle \\
&= \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma}(\mathbf{r}) \chi_{\gamma;\sigma'}(\mathbf{r}') \quad , \quad (6.1.5)
\end{aligned}$$

and for the exchange term

$$\begin{aligned}
& \left\{ \langle \chi_\alpha^{(1)} | \otimes \langle \chi_\gamma^{(2)} | \right\} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \left\{ | \chi_\gamma^{(1)} \rangle \otimes | \chi_\alpha^{(2)} \rangle \right\} \\
&= \sum_{\sigma\sigma'} \sum_{\sigma''\sigma'''} \int d^3\mathbf{x} \int d^3\mathbf{x}' \int d^3\mathbf{x}'' \int d^3\mathbf{x}''' \langle \chi_\alpha^{(1)} | \mathbf{x}, \sigma \rangle \langle \chi_\gamma^{(2)} | \mathbf{x}', \sigma' \rangle \\
&\quad \{ \langle \mathbf{x}, \sigma | \otimes \langle \mathbf{x}', \sigma' | \} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \{ | \mathbf{x}'', \sigma'' \rangle \otimes | \mathbf{x}''', \sigma''' \rangle \} \\
&\quad \langle \mathbf{x}'', \sigma'' | \chi_\gamma^{\{1\}} \rangle \langle \mathbf{x}''', \sigma''' | \chi_\alpha^{\{2\}} \rangle \\
&= \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r}) \quad . \quad (6.1.6)
\end{aligned}$$

In Eqs. (6.1.5) and (6.1.6) two of the spin sums and real space integrals have disappeared due to the spin independence as well as the locality of the potential. Note that the states $|\chi_\alpha\rangle$ might be mixed spin states and thus have non-zero projections onto both spin channels. Summarizing we obtain the result

$$\begin{aligned}
& \langle H_0 \rangle_\psi \\
&= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} \chi_{\alpha;\sigma}(\mathbf{r}) \\
&\quad + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\alpha\gamma} (1 - \delta_{\alpha\gamma}) \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\
&\quad \left[\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma}(\mathbf{r}) \chi_{\gamma;\sigma'}(\mathbf{r}') \right. \\
&\quad \left. - \chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r}) \right] \quad , \\
&\hspace{15em} (6.1.7)
\end{aligned}$$

which is the Hartree-Fock counterpart of Eq. (4.4.3). Note that, as mentioned above, we have kept the factor $(1 - \delta_{\alpha\gamma})$ to explicitly exclude the unphysical self-interaction.

Having calculated the energy functional with the correctly antisymmetrized many-body states we proceed in much the same way as in section 4.4. We thus vary the expression (6.1.7) with respect to the single particle state χ_α^* and seek for the zero's of the first variation. As before, this involves variation of both the function χ_α^* and its complex conjugate χ_α . If we want to vary all single particle states as well as their complex conjugate states independently, we need to enforce the normalization condition for χ_α^* and χ_α and write the variational expression as

$$\delta \left(\langle H_0 \rangle_\psi - \sum_\alpha \epsilon_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\alpha;\sigma}(\mathbf{r}) \right) \stackrel{!}{=} 0 \quad . \quad (6.1.8)$$

Combining this with the energy functional (6.1.7) we obtain

$$\begin{aligned} 0 \stackrel{!}{=} & \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \delta\chi_{\alpha;\sigma}^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} \chi_{\alpha;\sigma}(\mathbf{r}) \\ & + \frac{1}{4\pi\epsilon_0} \sum_{\alpha\gamma} (1 - \delta_{\alpha\gamma}) \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\ & \quad \delta\chi_{\alpha;\sigma}^*(\mathbf{r}) \left[\chi_{\gamma;\sigma'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma}(\mathbf{r}) \chi_{\gamma;\sigma'}(\mathbf{r}') \right. \\ & \quad \quad \left. - \chi_{\gamma;\sigma'}^*(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r}) \right] \\ & - \sum_\alpha \epsilon_\alpha \sum_\sigma \int d^3\mathbf{r} \delta\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\alpha;\sigma}(\mathbf{r}) \quad . \end{aligned} \quad (6.1.9)$$

Again the factor $\frac{1}{2}$ in the two-particle contribution has vanished since the single particle orbitals appear twice in the double sum. As for the derivation of the Hartree equations we employ the fact that the variational expression (6.1.9) holds for arbitrary variations as well as for any dependence on the vector \mathbf{r} . This gives rise to the Hartree-Fock equations

$$\begin{aligned} 0 \stackrel{!}{=} & \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) - \epsilon_\alpha \right. \\ & + \frac{e^2}{4\pi\epsilon_0} \sum_\gamma (1 - \delta_{\alpha\gamma}) \sum_{\sigma'} \int d^3\mathbf{r}' \\ & \quad \left. \left[\frac{\chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\gamma;\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{\chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \frac{\chi_{\alpha;\sigma'}(\mathbf{r}')}{\chi_{\alpha;\sigma}(\mathbf{r})} \right] \right] \chi_{\alpha;\sigma}(\mathbf{r}) \quad , \end{aligned} \quad (6.1.10)$$

which have the character of single particle equations with eigenvalues ϵ_α and eigenfunctions $\chi_{\alpha;\sigma}(\mathbf{r})$ as projected onto the spin eigenstates and given at position \mathbf{r} . In the same manner as in Sec. 4.4 we thus write the Hartree-Fock

equations as

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) = \epsilon_{\alpha}\chi_{\alpha;\sigma}(\mathbf{r}) \quad , \quad (6.1.11)$$

with the effective single particle potential determined by

$$v_{eff,\sigma}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{x,\sigma}(\mathbf{r}) \quad . \quad (6.1.12)$$

Here the first term designates the potential due to the ions and

$$\begin{aligned} v_H(\mathbf{r})\chi_{\alpha;\sigma}(\mathbf{r}) &= \frac{e^2}{4\pi\epsilon_0} \sum_{\gamma} (1 - \delta_{\alpha\gamma}) \sum_{\sigma'} \int d^3\mathbf{r}' \frac{|\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma}(\mathbf{r}) \\ &\approx \frac{e^2}{4\pi\epsilon_0} \sum_{\gamma} \sum_{\sigma'} \int d^3\mathbf{r}' \frac{|\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma}(\mathbf{r}) \\ &= \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma}(\mathbf{r}) \quad , \end{aligned} \quad (6.1.13)$$

$$\begin{aligned} v_{x,\sigma}(\mathbf{r})\chi_{\alpha;\sigma}(\mathbf{r}) &= -\frac{e^2}{4\pi\epsilon_0} \sum_{\gamma} (1 - \delta_{\alpha\gamma}) \sum_{\sigma'} \int d^3\mathbf{r}' \frac{\chi_{\gamma;\sigma'}^*(\mathbf{r}')\chi_{\gamma;\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma'}(\mathbf{r}') \\ &\approx -\frac{e^2}{4\pi\epsilon_0} \sum_{\gamma} \sum_{\sigma'} \int d^3\mathbf{r}' \frac{\chi_{\gamma;\sigma'}^*(\mathbf{r}')\chi_{\gamma;\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma'}(\mathbf{r}') \\ &= -\frac{e^2}{4\pi\epsilon_0} \sum_{\sigma'} \int d^3\mathbf{r}' \frac{\rho_{\sigma\sigma'}(\mathbf{r};\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_{\alpha;\sigma'}(\mathbf{r}') \end{aligned} \quad (6.1.14)$$

define the Hartree as well as the spin-dependent exchange potential. The latter usually is designated by the index x . In the respective second and third lines of Eqs. (6.1.13) and (6.1.14) we have included the self-interaction terms $\delta_{\alpha\gamma}$, which fact allowed to express the Hartree and exchange potential, respectively, in terms of the density and the density matrix as specified in Eqs. (5.7.17) to (5.7.19) rather than the single particle orbitals. In this context we made use of the fact that the summations in the respective second lines include only the occupied single particle states. Nevertheless, we point out once more that expressing the Hartree and exchange potential in terms of the density and the density matrix was possible only because these potentials are combined into the effective potential, where the diagonal terms cancel out. From this discussion it becomes, furthermore, obvious that within Hartree-Fock theory the effective potential (6.1.12) does not depend on the index of that state, to which it is applied. As a consequence, the potential is the same for all particles, this fact reflecting our aforementioned condition that no operator acting on a system of identical particles must label one of them.

The situation is different in the Hartree equations derived in Sec. 4.4, which deviate from the Hartree-Fock result by the omittance of the exchange contribution. For this reason, the self-interaction term strictly speaking must not be included in the Hartree potential and the effective potential entering the Hartree equations thus depends on the state index.

Being a consequence of the identity of particles, hence, of the antisymmetrization of the fermionic many-body function, the exchange contribution is of completely quantum mechanical nature and thus can not be understood within classical mechanics. In addition, the exchange potential is a non-local potential since it contains the wave function $\chi_{\alpha;\sigma}(\mathbf{r}')$ at positions $\mathbf{r}' \neq \mathbf{r}$. Obviously, the latter fact complicates the solution of the Hartree-Fock equations considerably.

It is important to note that the effective potential (6.1.12) represents an Hermitian operator. This becomes obvious from calculating the matrix elements

$$\begin{aligned}
& \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) v_{eff,\sigma}(\mathbf{r}) \chi_{\beta;\sigma}(\mathbf{r}) \\
&= \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) v_{ext}(\mathbf{r}) \chi_{\beta;\sigma}(\mathbf{r}) \\
&\quad + \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \chi_{\beta;\sigma}(\mathbf{r}) \\
&\quad - \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \sum_{\sigma'} \int d^3\mathbf{r}' \frac{\rho_{\sigma\sigma'}(\mathbf{r};\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \chi_{\beta;\sigma'}(\mathbf{r}') \\
&= \left[\sum_{\sigma} \int d^3\mathbf{r} \chi_{\beta;\sigma}^*(\mathbf{r}) v_{ext}(\mathbf{r}) \chi_{\alpha;\sigma}(\mathbf{r}) \right. \\
&\quad + \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma} \int d^3\mathbf{r} \chi_{\beta;\sigma}^*(\mathbf{r}) \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \chi_{\alpha;\sigma}(\mathbf{r}) \\
&\quad \left. - \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma'} \int d^3\mathbf{r}' \chi_{\beta;\sigma'}^*(\mathbf{r}') \sum_{\sigma} \int d^3\mathbf{r} \frac{\rho_{\sigma'\sigma}(\mathbf{r}';\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \chi_{\alpha;\sigma}(\mathbf{r}) \right]^* \\
&= \left[\sum_{\sigma} \int d^3\mathbf{r} \chi_{\beta;\sigma}^*(\mathbf{r}) v_{eff,\sigma}(\mathbf{r}) \chi_{\alpha;\sigma}(\mathbf{r}) \right]^* . \tag{6.1.15}
\end{aligned}$$

Here we have used the respective third lines of Eqs. (6.1.13) and (6.1.14) as well as Eq. (5.7.17). As a consequence of Eq. (6.1.15) the eigenvalues ϵ_{α} turn out to be real and the eigenfunctions χ_{α} are indeed pairwise orthogonal.

In the same manner as the effective potential (4.4.8) entering the Hartree equations (4.4.7) the effective potential (6.1.12) of the Hartree-Fock theory depends itself on the single particle wave functions or the charge density growing out of them. For this reason, the potential and the single particle wave functions again must be determined by iteration. Hence, one starts from an initial guess for the effective potential, inserts it into the Hartree-Fock equations (6.1.11) and evaluates a first approximation to the single particle wave functions χ_{α} , which in turn allow to calculate the effective potential via Eq. (6.1.12). Note, however, that, although the Hartree-Fock equations yield all single particle states, only the N lowest eigenstates are occupied and, hence, enter the electron density as well as the effective potential. The just described

cycle is iterated until self-consistency, when a required accuracy of the results is achieved.

Having the solutions of the Hartree-Fock equations at hand, we are able to calculate the eigenvalues from multiplying Eq. (6.1.11) from the left with $\chi_{\alpha;\sigma}^*(\mathbf{r})$, summing over spins and integrating over all space. Since the eigenfunctions are orthonormalized we obtain

$$\begin{aligned} \epsilon_\alpha &= \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\ &= \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\ &\quad + \frac{e^2}{4\pi\epsilon_0} \sum_\sigma \sum_\gamma (1 - \delta_{\alpha\gamma}) \sum_{\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\ &\quad \left[\frac{|\chi_{\alpha;\sigma}(\mathbf{r}')|^2 |\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] . \end{aligned} \quad (6.1.16)$$

Defining

$$S_\alpha = \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \quad (6.1.17)$$

as well as the Coulomb and exchange integral, respectively,

$$C_{\alpha,\gamma} = \frac{e^2}{4\pi\epsilon_0} \sum_\sigma \sum_{\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{|\chi_{\alpha;\sigma}(\mathbf{r})|^2 |\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} , \quad (6.1.18)$$

$$A_{\alpha,\gamma} = \frac{e^2}{4\pi\epsilon_0} \sum_\sigma \sum_{\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} , \quad (6.1.19)$$

we arrive at the result

$$\epsilon_\alpha = S_\alpha + \sum_\gamma (1 - \delta_{\alpha\gamma}) [C_{\alpha,\gamma} - A_{\alpha,\gamma}] . \quad (6.1.20)$$

With the above abbreviations the total energy functional (6.1.7) reads as

$$\langle H_0 \rangle_\psi = \sum_\alpha S_\alpha + \frac{1}{2} \sum_{\alpha\gamma} (1 - \delta_{\alpha\gamma}) [C_{\alpha,\gamma} - A_{\alpha,\gamma}] . \quad (6.1.21)$$

Combining Eqs. (6.1.20) and (6.1.21) we get the alternative expression

$$\langle H_0 \rangle_\psi = \sum_\alpha \epsilon_\alpha - \frac{1}{2} \sum_{\alpha\gamma} (1 - \delta_{\alpha\gamma}) [C_{\alpha,\gamma} - A_{\alpha,\gamma}] , \quad (6.1.22)$$

where the sums run over the occupied orbitals. According to Eq. (6.1.22) the energy functional thus falls into the sum of all single particle energies minus the so-called double counting terms. Inclusion of the latter is necessary, since the single sum over particle density times effective potential counts both the interaction of particle i with particle j as well as of particle j with particle i . As a consequence, the interaction via the effective potential is double counted and thus half of it has to be subtracted.

In order to get an impression about the influence of the exchange terms we insert into Eq. (6.1.22) the explicit formulas (6.1.16), (6.1.18) as well as (6.1.16) and note

$$\begin{aligned}
\langle H_0 \rangle_\psi &= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
&\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha\gamma} (1 - \delta_{\alpha\gamma}) \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\
&\quad \left[\frac{|\chi_{\alpha;\sigma'}(\mathbf{r}')|^2 |\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] \\
&= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
&\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha\gamma} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\
&\quad \left[\frac{|\chi_{\alpha;\sigma'}(\mathbf{r}')|^2 |\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] \\
&= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
&\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \left[\frac{\rho_\sigma(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{|\rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right], \tag{6.1.23}
\end{aligned}$$

where we used the exact cancellation of the self-interaction term in the sum of the direct and exchange integral as well as the spin-dependent density and density matrix with the latter given by Eq. (5.7.17). From the final expression it becomes clear that exchange integrals summed over all pairs of single particle states results in a positive definite contribution. As a consequence, on inclusion of the exchange integrals the total energy will be lowered. In particular, the Hartree-Fock total energy is lower than the Hartree energy.

For the following discussions it will be useful to have an expression of the Hartree-Fock ground state energy in terms of the density as well as the pair-correlation function at hand. To this end we start out from Eq. (6.1.21) and combine it the Eqs. (6.1.16), (6.1.18) as well as (6.1.16). In doing so we will again include the self-interaction term in both the direct and exchange contri-

bution. Using furthermore the definitions (5.7.23) and (5.7.31) we write

$$\begin{aligned}
\langle H_0 \rangle_\psi &= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
&+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha\gamma} (1 - \delta_{\alpha\gamma}) \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\
&\quad \left[\frac{|\chi_{\alpha;\sigma'}(\mathbf{r}')|^2 |\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] \\
&= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
&+ \sum_\sigma \int d^3\mathbf{r} v_{ext}(\mathbf{r}) \rho_\sigma(\mathbf{r}) \\
&+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \left[\frac{\rho_\sigma(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \frac{|\rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \right] \\
&= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) + \int d^3\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \\
&+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{P_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&= \sum_\alpha \sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) + \int d^3\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \\
&+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_\sigma(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} g_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}') \quad . \quad (6.1.24)
\end{aligned}$$

6.2 Exact relations

In this section we will derive some exact results, which provide some insight into Hartree-Fock theory and will be useful for the discussion of density functional theory lateron. These are, in particular, Brillouin's theorem and Koopmans' theorem.

The first of these theorems is based on the variational procedure and a particular ansatz of the many-body wave function. To be specific we calculate the variation of the energy functional explicitly as

$$\frac{\partial}{\partial \eta} \frac{\langle \psi_- + \eta \chi | H_0 | \psi_- \rangle}{\langle \psi_- + \eta \chi | \psi_- \rangle} \Big|_{\eta=0} \stackrel{!}{=} 0 \quad . \quad (6.2.1)$$

The choice of the wave function in the bra state is subject to the condition that

1. $|\psi_- + \eta \chi\rangle$ like $|\psi_- \rangle$ must be a Slater determinant and
2. $|\psi_- + \eta \chi\rangle$ must deviate from $|\psi_- \rangle$ only with respect to changing one single particle orbital.

We are thus able to write the modified many-body state as

$$\begin{aligned}
|\psi_- + \eta\chi\rangle &= (N!)^{-\frac{1}{2}} \cdot \begin{vmatrix} |\chi_{\alpha_1}^{(1)}\rangle & |\chi_{\alpha_1}^{(2)}\rangle & \cdots & |\chi_{\alpha_1}^{(N)}\rangle \\ |\chi_{\alpha_2}^{(1)}\rangle & |\chi_{\alpha_2}^{(2)}\rangle & \cdots & |\chi_{\alpha_2}^{(N)}\rangle \\ \vdots & \vdots & & \vdots \\ |\chi_{\alpha_p}^{(1)} + \eta\bar{\chi}\rangle & |\chi_{\alpha_p}^{(2)} + \eta\bar{\chi}\rangle & \cdots & |\chi_{\alpha_p}^{(N)} + \eta\bar{\chi}\rangle \\ \vdots & \vdots & & \vdots \\ |\chi_{\alpha_N}^{(1)}\rangle & |\chi_{\alpha_N}^{(2)}\rangle & \cdots & |\chi_{\alpha_N}^{(N)}\rangle \end{vmatrix} \\
&= (N!)^{-\frac{1}{2}} \cdot \begin{vmatrix} |\chi_{\alpha_1}^{(1)}\rangle & |\chi_{\alpha_1}^{(2)}\rangle & \cdots & |\chi_{\alpha_1}^{(N)}\rangle \\ |\chi_{\alpha_2}^{(1)}\rangle & |\chi_{\alpha_2}^{(2)}\rangle & \cdots & |\chi_{\alpha_2}^{(N)}\rangle \\ \vdots & \vdots & & \vdots \\ |\chi_{\alpha_p}^{(1)}\rangle & |\chi_{\alpha_p}^{(2)}\rangle & \cdots & |\chi_{\alpha_p}^{(N)}\rangle \\ \vdots & \vdots & & \vdots \\ |\chi_{\alpha_N}^{(1)}\rangle & |\chi_{\alpha_N}^{(2)}\rangle & \cdots & |\chi_{\alpha_N}^{(N)}\rangle \end{vmatrix} \\
&\quad + \eta \cdot (N!)^{-\frac{1}{2}} \cdot \begin{vmatrix} |\chi_{\alpha_1}^{(1)}\rangle & |\chi_{\alpha_1}^{(2)}\rangle & \cdots & |\chi_{\alpha_1}^{(N)}\rangle \\ |\chi_{\alpha_2}^{(1)}\rangle & |\chi_{\alpha_2}^{(2)}\rangle & \cdots & |\chi_{\alpha_2}^{(N)}\rangle \\ \vdots & \vdots & & \vdots \\ |\bar{\chi}\rangle & |\bar{\chi}\rangle & \cdots & |\bar{\chi}\rangle \\ \vdots & \vdots & & \vdots \\ |\chi_{\alpha_N}^{(1)}\rangle & |\chi_{\alpha_N}^{(2)}\rangle & \cdots & |\chi_{\alpha_N}^{(N)}\rangle \end{vmatrix} .
\end{aligned} \tag{6.2.2}$$

Next we use for $|\bar{\chi}\rangle$ successively all the single particle wave functions. In case that $|\bar{\chi}\rangle$ is one of the occupied orbitals, i.e. $|\bar{\chi}\rangle = |\chi_{\alpha_i}\rangle$ for $i = 1, \dots, N$, the variation (6.2.1) vanishes trivially, because the second Slater determinant itself vanishes (for $i \neq p$, where p is the orbital indicated in Eq. (6.2.2)) or the sum of both Slater determinants is proportional to the original one (for $i = p$) with the proportionality factor $(1 + \eta)$ canceling out from Eq. (6.2.1). Hence, $|\bar{\chi}\rangle$ must be an unoccupied orbital ($i > N$) in order that the variation does not vanish. Replacing $|\chi_{\alpha_p}\rangle$ for $p \leq N$ by $|\chi_{\alpha_p} + \eta\chi_{\alpha_q}\rangle$ with $q > N$, hence, considering an excited state

$$|\chi\rangle = a_q^+ a_p |\psi_- \rangle =: |\psi_{qp}\rangle \quad \text{with } p \leq N < q \tag{6.2.3}$$

we obtain for the variational expression

$$\begin{aligned}
&\frac{\partial}{\partial \eta} \frac{\langle \psi_- | H_0 | \psi_- \rangle + \eta \langle \psi_{qp} | H_0 | \psi_- \rangle}{\langle \psi_- | \psi_- \rangle + \eta \langle \psi_{qp} | \psi_- \rangle} \Big|_{\eta=0} \\
&= \frac{\partial}{\partial \eta} [\langle \psi_- | H_0 | \psi_- \rangle + \eta \langle \psi_{qp} | H_0 | \psi_- \rangle]_{\eta=0} = \langle \psi_{qp} | H_0 | \psi_- \rangle \stackrel{!}{=} 0 \quad ,
\end{aligned} \tag{6.2.4}$$

where we have used the fact that $\langle \psi_{qp} | \psi_- \rangle = 0$ due to the orthogonality of the single particle states. According to this result the matrix elements of the Hamiltonian built with a Slater determinant and a state resulting from excitation of a single particle from this Slater determinant vanish. As a consequence, there will always be a gap in the excitation spectrum and metallic systems cannot be correctly described.

Finally, if we require that the Hartree-Fock Hamiltonian has the form of a single-particle operator, Eq. (6.2.4) implies that

$$\langle \chi_q | H_0 | \chi_p \rangle \stackrel{!}{=} 0 \quad \text{for } p \leq N < q \quad . \quad (6.2.5)$$

As a consequence, all matrix elements of the Hartree-Fock Hamiltonian built with an occupied and an unoccupied single-particle state vanish exactly.

Koopmans' theorem deals with the ionization energies I_κ of the interacting electron system as described by Hartree-Fock theory. We thus consider the difference of the energy functional of an N and an $N - 1$ particle system. Assuming that the particle is excited from the single particle state χ_κ we write, following Eq. (6.1.21), for the energy functional

$$\begin{aligned} \langle H_0 \rangle_\psi^{(N-1\kappa)} &= \sum_\alpha (1 - \delta_{\alpha\kappa}) S_\alpha \\ &\quad + \frac{1}{2} \sum_\alpha \sum_\gamma (1 - \delta_{\alpha\kappa})(1 - \delta_{\kappa\gamma})(1 - \delta_{\alpha\gamma}) [C_{\alpha,\gamma} - A_{\alpha,\gamma}] \\ &= \langle H_0 \rangle_\psi^{(N)} - S_\kappa - \frac{1}{2} \sum_\alpha (1 - \delta_{\alpha\kappa}) [C_{\alpha,\kappa} - A_{\alpha,\kappa}] \\ &\quad - \frac{1}{2} \sum_\gamma (1 - \delta_{\kappa\gamma}) [C_{\kappa,\gamma} - A_{\kappa,\gamma}] \\ &= \langle H_0 \rangle_\psi^{(N)} - S_\kappa - \sum_\alpha (1 - \delta_{\alpha\kappa}) [C_{\alpha,\kappa} - A_{\alpha,\kappa}] \\ &= \langle H_0 \rangle_\psi^{(N)} - \epsilon_\kappa \quad , \end{aligned} \quad (6.2.6)$$

where we have used the symmetry of the Coulomb and exchange integral with respect to the single-particle indices. We thus arrive at Koopmans' theorem

$$I_\kappa = \langle H_0 \rangle_\psi^{(N-1\kappa)} - \langle H_0 \rangle_\psi^{(N)} = -\epsilon_\kappa \quad . \quad (6.2.7)$$

The ionization energy thus arises simply as the negative eigenvalue ϵ_κ corresponding to the single particle state, from which the electron was removed. This is an important result in view of the fact that these eigenvalues, growing out of an approximate treatment of the electron-electron interaction, do not bear an exact physical meaning. However, our evaluation of ionization energies from Koopmans' theorem is based on the assumption that on removing an electron the states of the remaining electrons do not change drastically. In particular, the relaxation of the other electrons in response to the excitation of a single

particle is neglected. For this reason, the validity of the above assumption has to be questioned in real situations.

6.3 Hartree-Fock methods

Since the Hamiltonian (4.1.6) describing the system of electrons like the full Hamiltonian, Eqs. (2.1.1) to (2.1.4), does not explicitly depend on spin, it must commute with both the operator of the square as well as the z component of the total spin,

$$\left[H_0, \mathbf{S}^2 \right] = \left[H_0, S_z \right] \stackrel{!}{=} 0 \quad . \quad (6.3.1)$$

As a consequence, the Slater determinants (6.1.1) solving the Hartree-Fock Hamiltonian must be simultaneous eigenfunctions of the Hamiltonian and the above spin operators.

In Sec. 6.1, the eigenstates of the single-particle Hamiltonian were chosen to be of the form

$$\chi_\alpha(\mathbf{r}) = \sum_{\sigma} \varphi_{(\tilde{\alpha}, \sigma)}(\mathbf{r}) \chi_{\sigma} =: \sum_{\sigma} \chi_{(\tilde{\alpha}, \sigma)}(\mathbf{r}) \quad , \quad (6.3.2)$$

where the χ_{σ} denote the Pauli spinors

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \quad (6.3.3)$$

In Eq. (6.3.2) we have written the index α labelling the different eigenstates explicitly as a compose $\alpha = (\tilde{\alpha}, \sigma)$ of the spin index and all other quantum numbers characterizing these states. Since we allowed for mixed spin states in Sec. 6.1, the projections of the single-particle eigenstates onto the spinors,

$$\chi_{\alpha; \sigma'}(\mathbf{r}) = \chi_{\sigma'} \chi_{\sigma'}^* \sum_{\sigma} \chi_{(\tilde{\alpha}, \sigma)}(\mathbf{r}) = \varphi_{(\tilde{\alpha}, \sigma')}(\mathbf{r}) \chi_{\sigma'} = \chi_{(\tilde{\alpha}, \sigma')}(\mathbf{r}) \quad , \quad (6.3.4)$$

may yield non-zero results for both spin directions. As a consequence, the single Slater determinant (6.1.1) built from these eigenstates obviously is not an eigenstate of S_z with definite total spin and the commutation relations (6.3.1) are thus violated.

This erroneous situation can be cured by restricting the form of the single-particle orbitals from the very beginning such that the resulting Slater determinant is a simultaneous eigenstate of the total spin operators, \mathbf{S}^2 and S_z , as well as the Hamiltonian. To this end we define a fixed global spin quantization axis, to which the total spin operators as well as the single-particle spin operators, \mathbf{s}^2 and s_z , are referred. In addition, we enforce that the projections (6.3.4) of the single-particle states χ_{α} onto one of the spin states (6.3.3) are either one or zero. With this restriction the single-particle states thus assume the form

$$\chi_{\alpha}(\mathbf{r}) = \varphi_{(\tilde{\alpha}, \sigma)}(\mathbf{r}) \chi_{\sigma} =: \chi_{(\tilde{\alpha}, \sigma)}(\mathbf{r}) \quad (6.3.5)$$

and we obtain for the projection onto the spinors the result

$$\begin{aligned}\chi_{\alpha;\sigma'}(\mathbf{r}) &= \chi_{\sigma'}\chi_{\sigma'}^*\chi_{(\tilde{\alpha},\sigma)}(\mathbf{r}) \\ &= \varphi_{(\tilde{\alpha},\sigma')}(\mathbf{r})\chi_{\sigma'}\delta_{\sigma\sigma'} = \chi_{(\tilde{\alpha},\sigma')}(\mathbf{r})\delta_{\sigma\sigma'} \quad , \end{aligned} \quad (6.3.6)$$

which contrasts Eq. (6.3.4). Just for completeness we append the identity (5.7.3), which now reads as

$$\langle \mathbf{x}, \sigma | \chi_{\alpha} \rangle = \langle \mathbf{x}, \sigma | \chi_{(\tilde{\alpha},\sigma')} \rangle = \chi_{(\tilde{\alpha},\sigma')}(\mathbf{x})\delta_{\sigma\sigma'} \quad . \quad (6.3.7)$$

Eqs. (6.3.5) and (6.3.6) mark the starting point for the standard Hartree-Fock method, which is also termed the “Unrestricted Hartree-Fock” (UHF) method. Although this name seems to be somewhat misleading in view of the fact that the single-particle states (6.3.5) actually comprise less degrees of freedom than the states (6.3.2) the name “Unrestricted” was chosen in order to distinguish this method from the “Restricted Hartree-Fock” (RHF) methods, which impose even stronger conditions onto the single-particle wave functions.

The great conceptual as well as practical importance of the Unrestricted Hartree-Fock method justifies to take a closer look here. To this end we start out from the energy functional as given by Eq. (6.1.7) but now combine it with Eq. (6.3.5) for the single-particle states. Using the projections (6.3.6) we thus replace Eq. (6.1.7) by

$$\begin{aligned}\langle H_0 \rangle_{\psi} &= \sum_{\tilde{\alpha}} \sum_{\sigma} \int d^3\mathbf{r} \chi_{(\tilde{\alpha},\sigma)}^*(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right\} \chi_{(\tilde{\alpha},\sigma)}(\mathbf{r}) \\ &\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\tilde{\alpha}\tilde{\gamma}} \sum_{\sigma\sigma'} (1 - \delta_{\tilde{\alpha}\tilde{\gamma}}\delta_{\sigma\sigma'}) \int d^3\mathbf{r} \int d^3\mathbf{r}' \\ &\quad \left[\chi_{(\tilde{\alpha},\sigma)}^*(\mathbf{r})\chi_{(\tilde{\gamma},\sigma')}^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \chi_{(\tilde{\alpha},\sigma)}(\mathbf{r})\chi_{(\tilde{\gamma},\sigma')}(\mathbf{r}') \right. \\ &\quad \left. - \delta_{\sigma\sigma'} \chi_{(\tilde{\alpha},\sigma)}^*(\mathbf{r})\chi_{(\tilde{\gamma},\sigma')}^*(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \chi_{(\tilde{\alpha},\sigma')}(\mathbf{r}')\chi_{(\tilde{\gamma},\sigma)}(\mathbf{r}) \right] \quad . \end{aligned} \quad (6.3.8)$$

Note that the sums over spins, although still present, now are part of the summations over all single-particle eigenstates. While Eq. (6.3.8) formally is almost identical to the general expression (6.1.7) an important difference arises for the exchange term. Due to the exchange of particles this term comprises the projections of the single-particle states χ_{α} and χ_{γ} onto both the spins σ and σ' in Eq. (6.1.7). In the present context the restriction (6.3.6) on pure spin states thus enforces $\sigma = \sigma'$ in the exchange contribution, which we accounted for by adding an extra Kronecker δ .

Now proceeding along the same lines as in Sec. 6.1 for the general Hartree-Fock method we enforce the normalization of the single-particle states and

formulate the variational expression as

$$\delta \left(\langle H_0 \rangle_\psi - \sum_{\bar{\alpha}\sigma} \epsilon_{(\bar{\alpha},\sigma)} \int d^3\mathbf{r} \chi_{(\bar{\alpha},\sigma)}^*(\mathbf{r}) \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) \right) \stackrel{!}{=} 0 \quad (6.3.9)$$

and, finally, arrive at the Hartree-Fock equations for the standard method,

$$\begin{aligned} 0 \stackrel{!}{=} & \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) - \epsilon_{(\bar{\alpha},\sigma)} \right. \\ & + \frac{e^2}{4\pi\epsilon_0} \sum_{\tilde{\gamma}\sigma'} (1 - \delta_{\bar{\alpha}\tilde{\gamma}} \delta_{\sigma\sigma'}) \int d^3\mathbf{r}' \\ & \left. \left[\frac{\chi_{(\tilde{\gamma},\sigma')}^*(\mathbf{r}') \chi_{(\tilde{\gamma},\sigma')}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right. \right. \\ & \left. \left. - \delta_{\sigma\sigma'} \frac{\chi_{(\tilde{\gamma},\sigma')}^*(\mathbf{r}') \chi_{(\tilde{\gamma},\sigma')}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{\chi_{(\bar{\alpha},\sigma')}(\mathbf{r}')}{\chi_{(\bar{\alpha},\sigma)}(\mathbf{r})} \right] \right] \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) \quad . \end{aligned} \quad (6.3.10)$$

Again, these are single-particle equations with eigenvalues $\epsilon_{(\bar{\alpha},\sigma)}$ and eigenfunctions $\chi_{(\bar{\alpha},\sigma)}(\mathbf{r})$. As in Sec. 6.1 we complement Eq. (6.3.10) by

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) = \epsilon_{(\bar{\alpha},\sigma)} \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) \quad , \quad (6.3.11)$$

where the effective single-particle potential is determined by

$$v_{eff,\sigma}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{x,\sigma}(\mathbf{r}) \quad , \quad (6.3.12)$$

with the last two terms, the Hartree and the exchange potential, explicitly given by

$$\begin{aligned} v_H(\mathbf{r}) \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) &= \frac{e^2}{4\pi\epsilon_0} \sum_{\tilde{\gamma}\sigma'} (1 - \delta_{\bar{\alpha}\tilde{\gamma}} \delta_{\sigma\sigma'}) \int d^3\mathbf{r}' \frac{|\chi_{(\tilde{\gamma},\sigma')}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) \\ &\approx \frac{e^2}{4\pi\epsilon_0} \sum_{\tilde{\gamma}\sigma'} \int d^3\mathbf{r}' \frac{|\chi_{(\tilde{\gamma},\sigma')}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) \\ &= \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) \quad , \quad (6.3.13) \\ v_{x,\sigma}(\mathbf{r}) \chi_{(\bar{\alpha},\sigma)}(\mathbf{r}) &= -\frac{e^2}{4\pi\epsilon_0} \sum_{\tilde{\gamma}\sigma'} (1 - \delta_{\bar{\alpha}\tilde{\gamma}} \delta_{\sigma\sigma'}) \delta_{\sigma\sigma'} \\ &\quad \int d^3\mathbf{r}' \frac{\chi_{(\tilde{\gamma},\sigma')}^*(\mathbf{r}') \chi_{(\tilde{\gamma},\sigma')}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_{(\bar{\alpha},\sigma')}(\mathbf{r}') \\ &\approx -\frac{e^2}{4\pi\epsilon_0} \sum_{\tilde{\gamma}\sigma'} \delta_{\sigma\sigma'} \int d^3\mathbf{r}' \frac{\chi_{(\tilde{\gamma},\sigma')}^*(\mathbf{r}') \chi_{(\tilde{\gamma},\sigma')}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_{(\bar{\alpha},\sigma')}(\mathbf{r}') \end{aligned}$$

$$= -\frac{e^2}{4\pi\epsilon_0} \sum_{\sigma'} \delta_{\sigma\sigma'} \int d^3\mathbf{r}' \frac{\rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \chi_{(\tilde{\alpha}, \sigma')}(\mathbf{r}') \quad . \quad (6.3.14)$$

Again we have added in the respective second and third lines of Eqs. (6.3.13) and (6.3.14) the self-interaction terms $\delta_{\tilde{\alpha}\tilde{\gamma}}\delta_{\sigma\sigma'}$ and expressed both potentials in terms of the density and the density matrix, Eqs. (5.7.17) to (5.7.19). Still, we refer to the warning expressed in the context of Eqs. (6.1.13) and (6.1.14).

Continuing our discussion about the interpretation of the exchange potential we point, in particular, to the fact that, within the restriction to spin eigenstates, this potential couples only electrons with same spin. This reflects the Pauli principle, which is likewise a consequence of the antisymmetrization of the many-body wave function and requires particles of same spin to stay away from each other. Due to the repulsive Coulomb interaction between the electrons this mechanism at the same time reduces the total energy and for this reason the exchange potential comes with a minus sign.

The previous discussion bears an important aspect, which stems from the spin dependence of the exchange potential acting only between electrons with like spin. Obviously, the aforementioned energy reduction will be most effective if all the electrons carry the same spin, say $\sigma = +\frac{1}{2}$. Such a complete polarization of the electron spins macroscopically gives rise to stable ferromagnetic order. However, we may ask, why only few materials show this behaviour in nature. This is again a consequence of the Pauli principle, since with only $\sigma = +\frac{1}{2}$ states occupied orbitals with higher single particle energies must be filled, which fact causes increase of the kinetic energy, hence, of the total energy. We thus realize that the appearance of magnetic order is influenced by the balance between kinetic and exchange energy contributions. Although this balance depends on the details of the electronic states (“the electronic structure”) a rather simple criterion, the Stoner criterion for ferromagnetism, can be derived already from the following qualitative consideration. Let us start from the unpolarized (“reference”) state, where equal numbers of spin up ($\sigma = +\frac{1}{2}$) and spin down ($\sigma = -\frac{1}{2}$) electrons exist. Next suppose that a large amount of single particle spin up states are available at energies just above the highest occupied states. In this case electron polarization, i.e. letting the electrons populate these spin up states rather than the originally occupied spin down states will keep the kinetic energy price at a minimum while nevertheless reducing the exchange energy. As a consequence, magnetism is likely to occur in this situation. The Stoner criterion thus states that, if the density of states at the Fermi energy separating the occupied from the unoccupied states exceeds a certain value, ferromagnetic order will result.

We illustrate this criterion with the densities of states of nonmagnetic chromium and iron as calculated using the augmented spherical wave method. The results are shown in Fig. 6.1. While the total DOS of Cr has a minimum near the Fermi energy, we witness a rather sharp peak and a high DOS at E_F in the case of iron. According to the Stoner criterion this situation would favor ferromagnetic order in Fe, which indeed is observed. In contrast, chromium does not undergo a ferromagnetic phase transition.

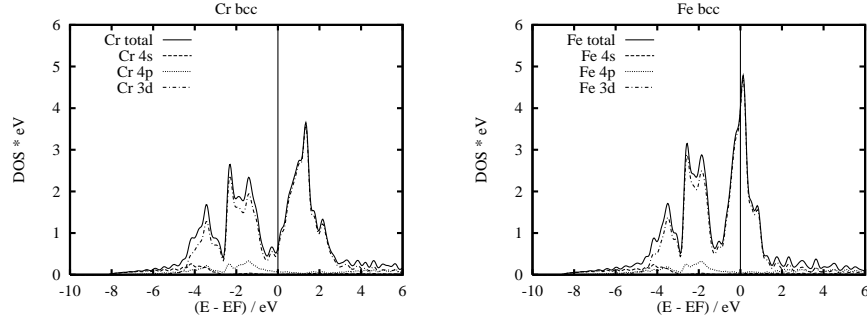


Figure 6.1: Total and partial densities of states (DOS) per atom of Cr and Fe.

As already mentioned the unrestricted Hartree-Fock method is contrasted with the restricted Hartree-Fock (RHF) method, which enforces additional symmetries. Examples are angular momentum eigenstates in atoms or the requirement of spin degeneracy in case of materials without magnetic order. As is obvious from the variational character of Hartree-Fock theory such restrictions cause an increase of the total energy as compared to the total unrestricted case. For this reasons we are faced with the fact that the solutions of lowest energy, while being nearest to the ground state, display the wrong symmetry and those solutions with the correct symmetry have elevated total energies. This is sometimes called the “symmetry dilemma” of Hartree-Fock theory. One way out are projection methods, where the solutions of correct symmetry are projected out after an unrestricted Hartree-Fock calculation has been performed.

A special implementation of great practical importance is the Hartree-Fock-Roothaan method. In this method the single particle wave functions are expanded in a set of basis functions,

$$\chi_{(\tilde{\alpha},\sigma)}(\mathbf{r}) = \sum_{\mu} c_{(\tilde{\alpha},\sigma)}^{\mu} \psi_{(\mu,\sigma)}(\mathbf{r}) \quad , \quad (6.3.15)$$

where α comprises a set of quantum numbers as, e.g., the angular momentum, a \mathbf{q} vector characterizing a plane wave or the atomic site, at which the respective function is centered in case of localized functions. The functions $\psi_{(\mu,\sigma)}(\mathbf{r})$ themselves are assumed to be analytically known and to depend on only few parameters. Inserting the expansion (6.3.15) into the general Hartree-Fock equation (6.3.15) we arrive at

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] \sum_{\nu} c_{(\tilde{\alpha},\sigma)}^{\nu} \psi_{(\nu,\sigma)}(\mathbf{r}) = \epsilon_{(\tilde{\alpha},\sigma)} \sum_{\nu} c_{(\tilde{\alpha},\sigma)}^{\nu} \psi_{(\nu,\sigma)}(\mathbf{r}) \quad . \quad (6.3.16)$$

Multiplying from the left with a function $\psi_{(\mu,\sigma)}(\mathbf{r})$, defining

$$F^\sigma = \left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] , \quad (6.3.17)$$

and using the abbreviation

$$|\mu\rangle = \psi_{(\mu,\sigma)}(\mathbf{r}) \quad (6.3.18)$$

we arrive at the following matrix equation

$$\sum_{\nu} (\langle\mu|F^\sigma|\nu\rangle - \epsilon_{(\tilde{\alpha},\sigma)}\langle\mu|\nu\rangle) c_{(\tilde{\alpha},\sigma)}^\nu = 0 , \quad (6.3.19)$$

which poses a generalized eigenvalue problem of the type

$$\sum_{\nu} (F_{\mu\nu}^\sigma - \epsilon_{(\tilde{\alpha},\sigma)}S_{\mu\nu}) c_{(\tilde{\alpha},\sigma)}^\nu = 0 , \quad (6.3.20)$$

where

$$S_{\mu\nu} = \langle\mu|\nu\rangle \quad (6.3.21)$$

is the overlap matrix of the basis functions. Eq. (6.3.20) is called Roothaan's matrix equation [141]. We have thus arrived at an algebraic representation of the Hartree-Fock equations, which is easier to solve numerically than the integro-differential equation (6.1.14).

Usually, the Hartree-Fock-Roothaan method is based on a linear combination of atomic orbitals (LCAO) ansatz, where the functions are chosen as Slater type orbitals (STO's)

$$f(\mathbf{r}) = Nr^{n-1}e^{\zeta r}Y_{lm}(\hat{\mathbf{r}}) . \quad (6.3.22)$$

Here $r = |\mathbf{r}|$, $N = ((2n)!)^{-1/2} (2\zeta)^{n+1/2}$ is the normalization factor, n, l, m denote the principal, angular momentum, as well as the magnetic quantum number, respectively, and $Y_{lm}(\hat{\mathbf{r}})$ denotes a spherical harmonics. When only one ζ is chosen (single ζ basis), its value is selected as

$$\zeta = \frac{Z - s}{n^*} , \quad (6.3.23)$$

where Z is the atomic number. The screening constant s and the effective principal quantum number n^* are evaluated from empirical rules formulated by Slater [150]. While STO's provide a good representation of the wave function especially near the nucleus, the calculation of one- and two-center integrals is quite cumbersome.

A different choice consists of Gaussian type orbitals (GTO's) of the Cartesian form,

$$f(\mathbf{r}) = Nx^jx^jy^jy^jz^jz^je^{\zeta r^2} . \quad (6.3.24)$$

Here N again is a normalization factor. GTO's have the distinct advantage that three- and four-center integrals can be reduced to much simpler two-center

integrals since the product of two GTO's at different centers can be written as a single GTO centered between the two centers. Finally, there exist Gaussian lobe functions, which are Gaussians displaced from the atomic center in order to simulate orbitals of angular momentum $l > 0$. A problem with GTO's results from the fact that they reflect the atomic wave functions less accurately than STO's and, hence, usually 3-4 more GTO's are needed than STO's. The latter fact, of course, increases the computer time considerably.

6.4 Concluding remarks

Both the Hartree and Hartree-Fock approach approximate the ground state by a single product and a single Slater determinant, respectively. Although the variational procedure gives rise to optimal single particle functions *within* this approach, the underlying idea is still rather crude if a considerable number of many-body states exist at slightly elevated energies. Such states are completely ignored and, obviously, a single Slater determinant does not suffice in such cases. Another disadvantage of using only a single Slater determinant became clear from the derivation of Brillouin's theorem, which showed that even for metallic systems a finite gap between occupied and empty electron states appears. Next, while neglecting electronic correlations completely, Hartree-Fock theory takes the exchange between the electron fully into account. As a consequence, optical band gaps usually come out much too large. Nevertheless, the exact treatment of exchange may promote new ideas for an improved consideration of this contribution in density functional theory based approaches. Finally, the restriction of the Hartree-Fock method to single Slater determinants led to severe difficulties with respect to the symmetry properties of the many-body wave function. For this reason, the correct symmetry had to be enforced by restricting the single particle wave functions or their combination in the Slater determinant. Of course, this is unsatisfactory.

The aforementioned deficiency could be cured, in principle, by using instead of the single Slater determinant a linear combination of them. Such a "configuration interaction" (CI) improves the situation a lot and usually leads close to the exact result. Nevertheless, in practice the enormous computer requirements coming along with CI calculations limit the method to systems with only few electrons. Moreover, the rather complicated nature of the obtained wave function hinders a simple interpretation of the results.

Chapter 7

The homogeneous electron gas

7.1 The Jellium model

In Sec. 3.1 we have learned about the Sommerfeld model, which was proposed to describe properties of elemental metals. In this model electron-electron interactions are throughout neglected and the presence of the ions is completely ignored. This latter step was justified by the screening of the nuclei by the core electrons, which considerably decreases the effective ionic potential. In addition, the thus reduced electron-ion interaction was thought to be cancelled by the electron-electron interaction for charge neutrality reasons. As outlined in Sec. 3.1 the Sommerfeld model is characterized by parabolic band dispersions as well as the resulting square root behaviour of the density of states. While we found, in general, surprisingly good agreement of this approach with the band structures and densities of states of the simple metals as presented in Sec. 3.2, we observed also considerable deviations as e.g. the lifting of band degeneracies or distinct minima in the density of states. These were fingerprints of both the imperfect screening of the nuclei and the electron-electron interactions.

In the present chapter we will go beyond the Sommerfeld model by including the electron-electron interaction. However, in doing so we will start on a Hartree-Fock level and only later on mention how correlations can be taken into account. Nevertheless, following the spirit of the Sommerfeld model we will, throughout in this chapter, still ignore the spatial structure of the potential created by the nuclei. In order to guarantee overall charge neutrality we thus have to smear out the ionic potentials and replace them by a constant positive background. The resulting caricature of the solid is denoted as the homogeneous electron gas or the Jellium model.

Of course, this model represents a severe approximation to the real situation. However, as a matter of fact it does account for many properties of the simple metals. Moreover, within Hartree-Fock theory an analytical solution is

possible, which avoids the iterative evaluation of the single particle wave functions. For this reason and, even more important, the Jellium model provides a highly valuable and sound basis for the local density approximation, where the effective potential for the inhomogeneous system is constructed from piecewise, hence, local homogeneous systems. To be more pictorial, in the inhomogeneous electron gas all space is artificially divided into small boxes. If small enough, in each box the electron density is well approximated by a constant density, hence, a homogeneous electron gas, for which the local potential can be constructed by the means to be discussed in this chapter. Finally, the results for all boxes are combined to the solution of the inhomogeneous electron gas.

In order to describe the homogeneous electron gas we start out again from the Hamiltonian (4.1.1), i.e.

$$\begin{aligned}
H_0 &= H_{ion-ion}(\{\mathbf{R}_\mu\}) + H_{el}(\{\mathbf{r}_i\}) + H_{ion-el}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\
&= \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 + v_{ext}(\mathbf{r}_i) \right] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\
&= \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 \right] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\nu \\ \mu \neq \nu}} \frac{Z_{val,\mu} Z_{val,\nu}}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} \\
&\quad - \frac{e^2}{4\pi\epsilon_0} \sum_\mu \sum_i \frac{Z_{val,\mu}}{|\mathbf{R}_\mu - \mathbf{r}_i|} + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad . \quad (7.1.1)
\end{aligned}$$

In the context of the homogeneous electron gas the ion-ion interaction, of course, reduces to a constant contribution to the Hamiltonian. At the same time the electron-ion interaction likewise represents just a constant potential seen by the electrons. However, as a closer inspection will reveal, the interaction of the positive ionic background with itself diverges for an infinite system if not properly combined with the neutralizing negative electronic charge density. We will thus have to carefully investigate all contributions to the Hamiltonian. In doing so we impose periodic Born-von Kármán boundary conditions as introduced in Sec. 2.6 and start from a discrete mesh of \mathbf{k} points within the reciprocal primitive cell as defined by Eq. (2.6.5). Only in the thermodynamic limit $N_{UC} \rightarrow \infty$, $\Omega = N_{UC}\Omega_{UC} \rightarrow \infty$, $N_{UC}/\Omega = const.$, to be performed at the end, the \mathbf{k} point mesh will become infinitesimally fine and the respective sums over \mathbf{k} points turn into integrals as was outlined in Sec. 2.7.

In general, the Coulombic ion-ion interaction is given by the second term in Eq. (7.1.1), i.e.

$$H_{ion-ion}(\{\mathbf{R}_\mu\}) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z_{val,\mu} Z_{val,\nu}}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} \quad , \quad (7.1.2)$$

where $Z_{val,\mu}$ is the number of valence electrons provided by the μ 'th ion. For

a constant ionic background the density assumes the form Eq. (3.1.6), i.e.

$$\rho = \frac{N}{N_{UC}\Omega_{UC}} = \frac{N}{\Omega} \quad , \quad (7.1.3)$$

where N is the total number of valence electrons, N_{UC} and Ω_{UC} denote the number and volume of the unic cells, respectively, and Ω is the volume of all space. We thus can rewrite the ion-ion interaction as

$$\begin{aligned} H_{ion-ion} &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho^2}{|\mathbf{r}-\mathbf{r}'|} e^{-\alpha|\mathbf{r}-\mathbf{r}'|} \\ &= \frac{1}{2} \frac{e^2\rho^2}{4\pi\epsilon_0} \Omega \int d^3\mathbf{r} \frac{e^{-\alpha|\mathbf{r}|}}{|\mathbf{r}|} \quad . \end{aligned} \quad (7.1.4)$$

Note the factor e^2 in front of the integral, which turns the squared density ρ^2 into a squared charge density $(e\rho)^2$. Furthermore, we point out that, by turning the double sum (7.1.2) into the double integral (7.1.4) we have actually ignored the condition $\mu \neq \nu$ coming with the former and, hence, erroneously included a self-interaction of the ionic system. This error will not be cured in the subsequent treatment of the homogeneous electron gas and must be accepted as an artefact of the underlying approximation. However, it causes a constant shift of the total potential and thus does not alter the final results.

In Eq. (7.1.4) we have introduced an additional damping factor $e^{-\alpha r}$ in order to suppress the divergence of the integral arising from the long range behaviour of the Coulomb potential. Of course, we will have to take the limit $\alpha \rightarrow \infty$ at the very end. The integral on the right hand side of Eq. (7.1.4) is just a special case of the Fourier transform of the screened Coulomb potential, which is calculated as

$$\begin{aligned} v_\alpha(\mathbf{q}) &= \int d^3\mathbf{r} \frac{e^{-\alpha|\mathbf{r}|}}{|\mathbf{r}|} e^{-i\mathbf{q}\mathbf{r}} \\ &= \int_0^\infty dr r^2 \int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \sin\vartheta \frac{e^{-\alpha r}}{r} e^{-iqr \cos\vartheta} \\ &= 2\pi \int_0^\infty dr r e^{-\alpha r} \int_{-1}^1 d \cos\vartheta e^{-iqr \cos\vartheta} \\ &= \frac{2\pi}{-iq} \int_0^\infty dr e^{-\alpha r} (e^{-iqr} - e^{iqr}) \\ &= \frac{4\pi}{q} \int_0^\infty dr e^{-\alpha r} \sin(qr) \\ &= \frac{4\pi}{q} \left[\frac{e^{-\alpha r}}{q^2 + \alpha^2} (-\alpha \sin(qr) - q \cos(qr)) \right]_0^\infty \\ &= \frac{4\pi}{q^2 + \alpha^2} \quad . \end{aligned} \quad (7.1.5)$$

Inserting this result for $\mathbf{q} = \mathbf{0}$ into Eq. (7.1.4) and using Eq. (7.1.3) we obtain

$$H_{ion-ion} = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} \quad , \quad (7.1.6)$$

which represents indeed a constant contribution to the Hamiltonian (7.1.1). However, as already mentioned above this term diverges for $\alpha \rightarrow 0$.

Next we turn to the electron-ion interaction, which is likewise of Coulombic nature and, hence, reads as

$$H_{ion-el} = -\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \int d^3\mathbf{r} \frac{\rho}{|\mathbf{r}-\mathbf{r}_i|} e^{-\alpha|\mathbf{r}-\mathbf{r}_i|} . \quad (7.1.7)$$

Again we have introduced the convergence factor $e^{-\alpha r}$. While the integral is evaluated in the same way as described in Eq. (7.1.5), the sum over the electrons turns into a factor N . Again using Eq. (7.1.3) we thus arrive at

$$H_{ion-el} = -\frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} , \quad (7.1.8)$$

which, when combined with the ion-ion interaction, Eq. (7.1.6), leads indeed to a partial cancellation. Inserting the intermediate results (7.1.6) and (7.1.8) into the original Hamiltonian (7.1.1) we thus write

$$\begin{aligned} H_0 &= H_{el}(\{\mathbf{r}_i\}) - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} \\ &= \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 \right] - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} + \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} . \end{aligned} \quad (7.1.9)$$

Although the Hamiltonian still contains a divergent term we will soon realize that also this remaining contribution is cancelled by part of the electron-electron interaction. Physically speaking this results from the required charge neutrality, which suppresses long range Coulomb interactions. Actually, the positive ionic background, while causing a constant external potential (the second term in Eq. (7.1.9) above) is balanced by a likewise constant negative electronic charge density, which even leads to a local compensation of charge and thus cancels the classical Coulomb interaction completely.

We proceed transferring the Hamiltonian (7.1.9) to the occupation number representation of the general form (5.4.26). Of course, the constant external potential suggests to opt for the plane waves (3.1.2) as a single-particle basis, hence,

$$\chi_{\mathbf{k}\sigma}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\mathbf{r}} \chi_{\sigma} = \langle \mathbf{r} | \mathbf{k}\sigma \rangle \quad (7.1.10)$$

with the spinors given by Eq. (6.3.3). Here we have in the last step appended the notation (5.7.3) of the real space representation. The Hamiltonian can thus be written as

$$H_0 = \sum_{\mathbf{k}_1 \mathbf{k}_2} \sum_{\sigma_1 \sigma_2} \langle \mathbf{k}_1 \sigma_1 | -\frac{\hbar^2}{2m} \nabla^2 | \mathbf{k}_2 \sigma_2 \rangle a_{\mathbf{k}_1 \sigma_1}^{\dagger} a_{\mathbf{k}_2 \sigma_2} - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2}$$

$$+\frac{1}{2} \sum_{\substack{\mathbf{k}_1 \mathbf{k}_2 \\ \mathbf{k}_3 \mathbf{k}_4}} \sum_{\substack{\sigma_1 \sigma_2 \\ \sigma_3 \sigma_4}} v(\mathbf{k}_1 \sigma_1, \mathbf{k}_2 \sigma_2, \mathbf{k}_3 \sigma_3, \mathbf{k}_4 \sigma_4) a_{\mathbf{k}_1 \sigma_1}^+ a_{\mathbf{k}_2 \sigma_2}^+ a_{\mathbf{k}_4 \sigma_4} a_{\mathbf{k}_3 \sigma_3} \quad , \quad (7.1.11)$$

with the Coulomb interaction matrix element given by

$$\begin{aligned} & v(\mathbf{k}_1 \sigma_1, \mathbf{k}_2 \sigma_2, \mathbf{k}_3 \sigma_3, \mathbf{k}_4 \sigma_4) \\ &= \frac{e^2}{4\pi\epsilon_0} \left\{ \langle (\mathbf{k}_1 \sigma_1)^{(1)} | \otimes \langle (\mathbf{k}_2 \sigma_2)^{(2)} | \right\} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ & \quad \left\{ |(\mathbf{k}_3 \sigma_3)^{(1)}\rangle \otimes |(\mathbf{k}_4 \sigma_4)^{(2)}\rangle \right\} \quad . \quad (7.1.12) \end{aligned}$$

With the plane wave basis the matrix elements arising from the kinetic energy contribution are easily calculated as

$$\begin{aligned} & \langle \mathbf{k}_1 \sigma_1 | -\frac{\hbar^2}{2m} \nabla^2 | \mathbf{k}_2 \sigma_2 \rangle \\ &= \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \langle \mathbf{k}_1 \sigma_1 | \mathbf{r} \rangle \langle \mathbf{r} | -\frac{\hbar^2}{2m} \nabla^2 | \mathbf{r}' \rangle \langle \mathbf{r}' | \mathbf{k}_2 \sigma_2 \rangle \\ &= -\frac{\hbar^2}{2m} \frac{1}{\Omega} \int d^3 \mathbf{r} e^{-i\mathbf{k}_1 \mathbf{r}} \nabla^2 e^{i\mathbf{k}_2 \mathbf{r}} \delta(\mathbf{r} - \mathbf{r}') \delta_{\sigma_1 \sigma_2} \\ &= \frac{\hbar^2 \mathbf{k}_2^2}{2m} \frac{1}{\Omega} \delta_{\sigma_1 \sigma_2} \int d^3 \mathbf{r} e^{-i(\mathbf{k}_1 - \mathbf{k}_2) \mathbf{r}} \\ &= \delta(\mathbf{k}_1 - \mathbf{k}_2) \delta_{\sigma_1 \sigma_2} \frac{\hbar^2 \mathbf{k}_2^2}{2m} \\ &=: \delta(\mathbf{k}_1 - \mathbf{k}_2) \delta_{\sigma_1 \sigma_2} \varepsilon_0(\mathbf{k}_2) \quad , \quad (7.1.13) \end{aligned}$$

which are, as expected, the single-particle energies of the Sommerfeld model.

In contrast, we obtain for the matrix elements (7.1.12) of the electron-electron interaction

$$\begin{aligned} & v(\mathbf{k}_1 \sigma_1, \mathbf{k}_2 \sigma_2, \mathbf{k}_3 \sigma_3, \mathbf{k}_4 \sigma_4) \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{\Omega^2} \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 \int d^3 \mathbf{r}_3 \int d^3 \mathbf{r}_4 \\ & \quad \langle \mathbf{k}_1 \sigma_1 | \mathbf{r}_1 \rangle \langle \mathbf{k}_2 \sigma_2 | \mathbf{r}_2 \rangle \\ & \quad \left\{ \langle \mathbf{r}_1^{(1)} | \otimes \langle \mathbf{r}_2^{(2)} | \right\} \frac{1}{|\mathbf{r}'_1 - \mathbf{r}'_2|} \left\{ | \mathbf{r}_3^{(1)} \rangle \otimes | \mathbf{r}_4^{(2)} \rangle \right\} \\ & \quad \langle \mathbf{r}_3 | \mathbf{k}_3 \sigma_3 \rangle \langle \mathbf{r}_4 | \mathbf{k}_4 \sigma_4 \rangle \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{\Omega^2} \delta_{\sigma_1 \sigma_3} \delta_{\sigma_2 \sigma_4} \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 e^{-i(\mathbf{k}_1 - \mathbf{k}_3) \mathbf{r}_1} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-i(\mathbf{k}_2 - \mathbf{k}_4) \mathbf{r}_2} \quad . \quad (7.1.14) \end{aligned}$$

In evaluating the integral we express the real space vectors \mathbf{r}_1 and \mathbf{r}_2 by

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad , \quad \mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \quad (7.1.15)$$

as

$$\mathbf{r}_1 = \mathbf{R} + \frac{1}{2}\mathbf{r} \quad , \quad \mathbf{r}_2 = \mathbf{R} - \frac{1}{2}\mathbf{r} \quad . \quad (7.1.16)$$

In addition, we introduce again the damping factor $e^{-\alpha r}$ in order to facilitate evaluation of the integral and arrive at

$$\begin{aligned} v_\alpha(\mathbf{k}_1\sigma_1, \mathbf{k}_2\sigma_2, \mathbf{k}_3\sigma_3, \mathbf{k}_4\sigma_4) \\ = \frac{e^2}{4\pi\epsilon_0} \frac{1}{\Omega^2} \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} \int d^3\mathbf{R} e^{-i(\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_4)\mathbf{R}} \\ \int d^3\mathbf{r} \frac{e^{-\alpha|\mathbf{r}|}}{|\mathbf{r}|} e^{-(i/2)(\mathbf{k}_1 - \mathbf{k}_3 - \mathbf{k}_2 + \mathbf{k}_4)\mathbf{r}} \quad . \quad (7.1.17) \end{aligned}$$

For the integral over \mathbf{R} we obtain

$$\int d^3\mathbf{R} e^{-i(\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_4)\mathbf{R}} = \Omega \delta(\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_4) \quad , \quad (7.1.18)$$

which is just the orthonormalization of the plane wave states (7.1.10). Inserting this into Eq. (7.1.17) and using the identity (7.1.5) we get

$$\begin{aligned} v_\alpha(\mathbf{k}_1\sigma_1, \mathbf{k}_2\sigma_2, \mathbf{k}_3\sigma_3, \mathbf{k}_4\sigma_4) \\ = \frac{e^2}{4\pi\epsilon_0} \frac{1}{\Omega} \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} \delta(\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_4) \int d^3\mathbf{r} \frac{e^{-\alpha|\mathbf{r}|}}{|\mathbf{r}|} e^{-i(\mathbf{k}_1 - \mathbf{k}_3)\mathbf{r}} \\ = \frac{e^2}{4\pi\epsilon_0} \frac{1}{\Omega} \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} \delta(\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_4) v_\alpha(\mathbf{k}_1 - \mathbf{k}_3) \\ = \frac{e^2}{4\pi\epsilon_0} \frac{4\pi}{\Omega} \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} \delta(\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_4) \frac{1}{(\mathbf{k}_1 - \mathbf{k}_3)^2 + \alpha^2} \quad . \quad (7.1.19) \end{aligned}$$

With this result at hand we write the electron-electron interaction part of the Hamiltonian (7.1.11) as

$$\begin{aligned} H_0^{(2)} &= \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mathbf{k}_1\mathbf{k}_2 \\ \mathbf{k}_3\mathbf{k}_4}} \sum_{\substack{\sigma_1\sigma_2 \\ \sigma_3\sigma_4}} \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_4} \delta(\mathbf{k}_1 - \mathbf{k}_3 + \mathbf{k}_2 - \mathbf{k}_4) v_\alpha(\mathbf{k}_1 - \mathbf{k}_3) \\ &\quad a_{\mathbf{k}_1\sigma_1}^+ a_{\mathbf{k}_2\sigma_2}^+ a_{\mathbf{k}_4\sigma_4} a_{\mathbf{k}_3\sigma_3} \\ &= \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}_1\mathbf{k}_3\mathbf{k}_4} \sum_{\sigma_1\sigma_2} v_\alpha(\mathbf{k}_1 - \mathbf{k}_3) a_{\mathbf{k}_1\sigma_1}^+ a_{\mathbf{k}_3+\mathbf{k}_4-\mathbf{k}_1\sigma_2}^+ a_{\mathbf{k}_4\sigma_2} a_{\mathbf{k}_3\sigma_1} \\ &= \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mathbf{k}\mathbf{p}\mathbf{q} \\ \sigma\sigma'}} v_\alpha(\mathbf{q}) a_{\mathbf{k}+\mathbf{q}\sigma}^+ a_{\mathbf{p}-\mathbf{q}\sigma'}^+ a_{\mathbf{p}\sigma'} a_{\mathbf{k}\sigma} \quad . \quad (7.1.20) \end{aligned}$$

In the last line of Eq. (7.1.20) we have appended a common alternative formulation based on renaming the indices according to

$$\mathbf{k}_3 = \mathbf{k} \quad , \quad \mathbf{k}_4 = \mathbf{p}$$

$$\begin{aligned} \sigma_1 = \sigma_3 = \sigma & \quad , & \quad \sigma_2 = \sigma_4 = \sigma' \\ \mathbf{k}_1 = \mathbf{k}_3 + \mathbf{q} = \mathbf{k} + \mathbf{q} & \quad , & \quad \mathbf{k}_2 = \mathbf{k}_4 + \mathbf{k}_3 - \mathbf{k}_1 = \mathbf{p} - \mathbf{q} \quad . \end{aligned} \quad (7.1.21)$$

Eventually, the previous considerations give rise to the following Hamiltonian of the Jellium model

$$\begin{aligned} H_0 &= \sum_{\mathbf{k}\sigma} \varepsilon_0(\mathbf{k}) a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} \\ &+ \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}_1 \mathbf{k}_3 \mathbf{k}_4} \sum_{\sigma_1 \sigma_2} v_0(\mathbf{k}_1 - \mathbf{k}_3) a_{\mathbf{k}_1 \sigma_1}^+ a_{\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_1 \sigma_2}^+ a_{\mathbf{k}_4 \sigma_2} a_{\mathbf{k}_3 \sigma_1} \\ &= \sum_{\mathbf{k}\sigma} \left[\varepsilon_0(\mathbf{k}) - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N}{\Omega} \frac{4\pi}{\alpha^2} \right] a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} \\ &+ \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mathbf{k} \mathbf{p} \mathbf{q} \\ \sigma \sigma'}} v_0(\mathbf{q}) a_{\mathbf{k} + \mathbf{q} \sigma}^+ a_{\mathbf{p} - \mathbf{q} \sigma'}^+ a_{\mathbf{p} \sigma'} a_{\mathbf{k} \sigma} \quad , \end{aligned} \quad (7.1.22)$$

with the matrix elements given by Eqs. (7.1.13) and (7.1.19).

Two points are worth mentioning at the end of this section: First, the plane wave basis already introduced for the Sommerfeld model obviously provides eigenstates of the kinetic energy operator, which has only diagonal matrix elements (7.1.13). Second, due to the dependence of the electron-electron interaction only on the difference between the respective electronic positions the number of independent \mathbf{k} summations in the final representation (7.1.22) reduces from four to three.

7.2 Perturbation theory for the Jellium model

In order to get some insight into the physical properties of the Jellium model we aim in a first step at the ground state energy. In doing so, we apply first order perturbation theory to the Hamiltonian (7.1.22). According to the variational principle this will give us an upper bound for the true value of the ground state energy. As the unperturbed system we choose the first contribution to the Hamiltonian, i.e. the kinetic energy term, which is just the Sommerfeld model studied in Sec. 3.1. We may thus fall back on the results derived there, in particular, the parabolic band dispersion (3.1.4), the square root behaviour (3.1.16) of the density of states as well as the results (3.1.9) and (3.1.11) given for the Fermi vector and energy, respectively. Furthermore, we recall the result (3.1.20) for the ground state energy.

Next we take into consideration the perturbation arising from the second contribution to the Hamiltonian (7.1.22) and calculate the first order energy correction as

$$\Delta E^{(1)} = \frac{1}{2} \sum_{\substack{\mathbf{k}_1 \mathbf{k}_3 \mathbf{k}_4 \\ \sigma_1 \sigma_2}}^{occ} v_0(\mathbf{k}_1 - \mathbf{k}_3) \langle \Psi_0 | a_{\mathbf{k}_1 \sigma_1}^+ a_{\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_1 \sigma_2}^+ a_{\mathbf{k}_4 \sigma_2} a_{\mathbf{k}_3 \sigma_1} | \Psi_0 \rangle$$

$$-\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} . \quad (7.2.1)$$

Apart from second term this energy correction is identical to the ground state expectation value of the two-particle contribution to the Hamiltonian H_0 as given by Eq. (7.1.1). We may thus use the general result (5.5.23) and write

$$\begin{aligned} \Delta E^{(1)} &= \frac{1}{2} \sum_{\substack{\mathbf{k}_1 \mathbf{k}_2 \mathbf{k}_3 \mathbf{k}_4 \\ \sigma_1 \sigma_2 \sigma_3 \sigma_4}}^{occ} v(\mathbf{k}_1 \sigma_1, \mathbf{k}_2 \sigma_2, \mathbf{k}_3 \sigma_3, \mathbf{k}_4 \sigma_4) \\ &\quad \left[\delta(\mathbf{k}_1 - \mathbf{k}_3) \delta_{\sigma_1 \sigma_3} \delta(\mathbf{k}_2 - \mathbf{k}_4) \delta_{\sigma_2 \sigma_4} \right. \\ &\quad \left. - \delta(\mathbf{k}_1 - \mathbf{k}_4) \delta_{\sigma_1 \sigma_4} \delta(\mathbf{k}_2 - \mathbf{k}_3) \delta_{\sigma_2 \sigma_3} \right] \\ &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} . \end{aligned} \quad (7.2.2)$$

Using Eq. (7.1.19) for the matrix element v_α we obtain for the first order energy correction

$$\begin{aligned} \Delta E^{(1)} &= -\frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mathbf{k}_1 \mathbf{k}_2 \\ \sigma_1 \sigma_2}}^{occ} v_\alpha(\mathbf{q} = \mathbf{0}) \\ &\quad - \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mathbf{k}_1 \mathbf{k}_3 \\ \sigma_1 \sigma_2 \sigma_3 \sigma_4}}^{occ} v_0(\mathbf{k}_1 - \mathbf{k}_3) \delta_{\sigma_1 \sigma_4} \delta_{\sigma_2 \sigma_3} \delta_{\sigma_1 \sigma_3} \delta_{\sigma_2 \sigma_4} \\ &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} \\ &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} - \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mathbf{k}_1 \mathbf{k}_3 \\ \sigma}}^{occ} v_0(\mathbf{k}_1 - \mathbf{k}_3) - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} \\ &= -\frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}\mathbf{q}\sigma}^{occ} v_0(\mathbf{q}) , \end{aligned} \quad (7.2.3)$$

where in the last lines we have used the alternative formulation in terms of \mathbf{k} and \mathbf{q} already used in Eq. (7.1.20) as well as the identity (7.1.5). Note that again the exchange term is diagonal in the spin indices.

In Eq. (7.2.3) we have used a finite screening factor α for the potential matrix element entering the direct term in order to allow for its explicit representation for $\mathbf{q} = \mathbf{0}$. This lead to the important result that the direct contribution exactly cancels the constant contribution to the Hamiltonian (7.1.22), which, as outlined in the previous section, grew out of the combined ion-ion and ion-electron interactions. This result seems quite plausible since, as already mentioned in Sec. 7.1, within the homogeneous electron gas we end up with local charge neutrality and, hence, all classical Coulomb interactions (ion-ion,

ion-electron, and electron-electron) compensate each other. The only remaining contribution is thus the non-classical exchange term. Note that this term, i.e. the last line of Eq. (7.2.3) contains an unrestricted \mathbf{q} summation. Of course, this facilitates the subsequent calculations a lot.

In the ground state of the Sommerfeld model, only states with wave vectors within the Fermi sphere are occupied and we are thus able to write Eq. (7.2.3) as

$$\Delta E^{(1)} = -\frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}\mathbf{q}\sigma} v_0(\mathbf{q}) \Theta(k_F - |\mathbf{k} + \mathbf{q}|) \Theta(k_F - |\mathbf{k}|) \quad , \quad (7.2.4)$$

where Θ denotes the Heaviside step function. In the thermodynamic limit the sum turns into an integral according to (2.7.2) and we obtain for the first order energy correction per particle

$$\begin{aligned} \frac{\Delta E^{(1)}}{N} &= -\frac{\Omega}{N(2\pi)^6} \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{k} \int d^3\mathbf{q} v_0(\mathbf{q}) \Theta(k_F - |\mathbf{k} + \mathbf{q}|) \Theta(k_F - |\mathbf{k}|) \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi\Omega}{N(2\pi)^6} \int d^3\mathbf{k} \int d^3\mathbf{q} \frac{1}{|\mathbf{q}|^2} \Theta(k_F - |\mathbf{k} + \mathbf{q}|) \Theta(k_F - |\mathbf{k}|) \quad , \end{aligned} \quad (7.2.5)$$

where we have inserted the Fourier component of the Coulomb potential, Eq. (7.1.5), and performed the summation over spins. Substituting

$$\mathbf{k} \rightarrow \mathbf{x} = \mathbf{k} + \frac{1}{2}\mathbf{q}$$

we write the integral as

$$\frac{\Delta E^{(1)}}{N} = -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi\Omega}{N(2\pi)^6} \int d^3\mathbf{q} \frac{1}{q^2} S(q) \quad , \quad (7.2.6)$$

where

$$S(q) = \Theta(k_F - \frac{q}{2}) \int d^3\mathbf{x} \Theta(k_F - |\mathbf{x} + \frac{\mathbf{q}}{2}|) \Theta(k_F - |\mathbf{x} - \frac{\mathbf{q}}{2}|) \quad (7.2.7)$$

is just the volume of the overlap region of two interpenetrating spheres with radius k_F , which are centered at $\frac{-\mathbf{q}}{2}$ and $\frac{+\mathbf{q}}{2}$, hence, are separated by a distance $q = |\mathbf{q}|$. The step function $\Theta(k_F - \frac{q}{2})$ ensures that the integral is finite only if the distance between the sphere centers is smaller than twice their radius, hence, if the spheres do actually overlap. The situation is visualized in Fig. 7.1, which displays a cut through the plane containing the centers of both spheres. For positive values of x the function circumscribing the overlap region is defined as

$$f(x) = \pm \sqrt{k_F^2 - \left(x + \frac{q}{2}\right)^2} \quad . \quad (7.2.8)$$

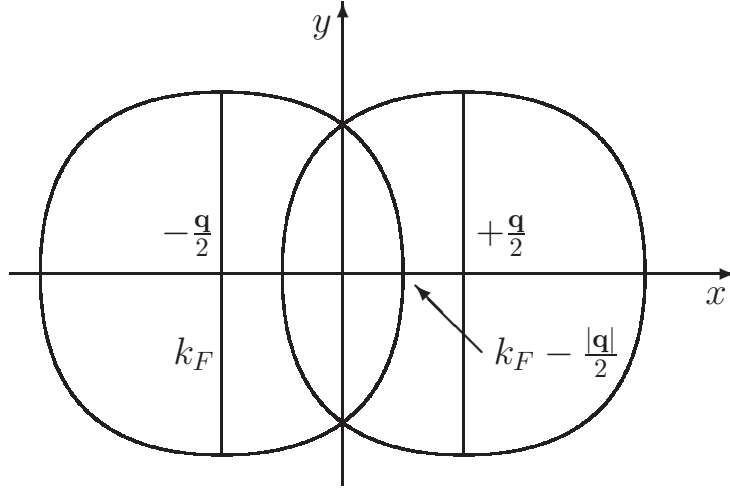


Figure 7.1: Cut through two overlapping spheres; the cut contains both sphere centers.

and the overlap volume is thus calculated in cylinder coordinates as

$$\begin{aligned}
S(q) &= 2 \cdot 2\pi\Theta(k_F - \frac{q}{2}) \int_0^{k_F - \frac{q}{2}} dx \int_0^{f(x)} dy y \\
&= 2 \cdot 2\pi\Theta(k_F - \frac{q}{2}) \int_0^{k_F - \frac{q}{2}} dx \frac{1}{2} \left[k_F^2 - \left(x + \frac{q}{2}\right)^2 \right] \\
&= 2\pi\Theta(k_F - \frac{q}{2}) \int_0^{k_F - \frac{q}{2}} dx \left[k_F^2 - x^2 - xq - \frac{q^2}{4} \right] \\
&= 2\pi\Theta(k_F - \frac{q}{2}) \left[\left(k_F^2 - \frac{q^2}{4}\right)x - \frac{1}{3}x^3 - \frac{1}{2}qx^2 \right]_0^{k_F - \frac{q}{2}} \\
&= 2\pi\Theta(k_F - \frac{q}{2}) \left[\left(k_F^2 - \frac{q^2}{4}\right) \left(k_F - \frac{q}{2}\right) \right. \\
&\quad \left. - \frac{1}{3} \left(k_F - \frac{q}{2}\right)^3 - \frac{1}{2}q \left(k_F - \frac{q}{2}\right)^2 \right] \\
&= 2\pi\Theta(k_F - \frac{q}{2}) \left[\frac{2}{3}k_F^3 - \frac{q}{2}k_F^2 + \frac{q^3}{24} \right] \\
&= \frac{4\pi}{3}\Theta(k_F - \frac{q}{2}) \left[k_F^3 - \frac{3}{4}k_F^2q + \frac{1}{16}q^3 \right] . \tag{7.2.9}
\end{aligned}$$

Inserting this result into Eq. (7.2.6) we get for the energy correction per particle

$$\frac{\Delta E^{(1)}}{N} = -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi\Omega}{N(2\pi)^6} \frac{(4\pi)^2}{3} \int_0^{2k_F} dq \left[k_F^3 - \frac{3}{4}k_F^2q + \frac{1}{16}q^3 \right]$$

$$\begin{aligned}
&= -\frac{e^2}{4\pi\epsilon_0} \frac{4\pi\Omega}{N(2\pi)^6} \frac{(4\pi)^2}{3} \left[2k_F^4 - \frac{3}{2}k_F^4 + \frac{1}{4}k_F^4 \right] \\
&= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2} \frac{\Omega}{N} \frac{1}{2\pi^3} k_F^4 \\
&= -\frac{3}{2\pi} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{1}{r_s/a_B} \text{Ryd} \\
&= -\frac{0.916}{r_s/a_B} \text{Ryd} \quad .
\end{aligned} \tag{7.2.10}$$

Finally, combining this expression with the ground state energy of the Sommerfeld model, Eq. (3.1.20), we arrive at the first order ground state energy per particle

$$\frac{E^{(1)}}{N} = \frac{E^{(0)} + \Delta E^{(1)}}{N} = \left[\frac{2.21}{(r_s/a_B)^2} - \frac{0.916}{r_s/a_B} \right] \text{Ryd} \quad . \tag{7.2.11}$$

The result is shown in Fig. 7.2, which clearly reveals an energy minimum at fi-

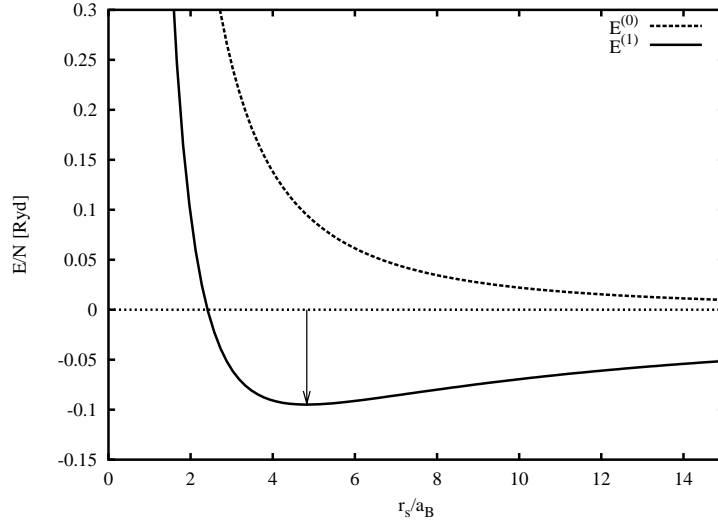


Figure 7.2: First order ground state energy per particle of the Jellium model; the dotted curve shows the zeroth order result arising from the Sommerfeld model.

nite values of r_s , hence at finite densities. This is contrasted by the Sommerfeld model, for which we have included the corresponding curve. Here a binding at finite values of r_s , hence, for finite electron densities does not occur. In general, while for small values of r_s the positive kinetic energy provides the major contribution to the ground state energy, for larger values of r_s the exchange term dominates and allows for metallic bonding. The minimum of the first order ground state energy is found at $r_s = 4.83a_B$ with an energy of -0.095 Ryd.

These values are close to the experimental values for Na, $r_s = 3.96a_B$ with an energy of -0.083 Ryd. To summarize, while the Sommerfeld model is unable to describe metallic bonding at all the inclusion of the exchange contribution to the total energy leads to a minimum ground state energy at finite values of r_s . Nevertheless, the calculated binding energies are still too small as compared to experiment due to the neglect of electron correlations.

7.3 Hartree-Fock approach to the Jellium model

It is instructive to complement the results for the Jellium model gained from first order perturbation theory by the corresponding solution as arising from Hartree-Fock theory as described in Chap. 6. To this end we assume that a fixed global spin quantization axis does exist and are thus able to apply the Hartree-Fock equations (6.3.11) coming with the unrestricted Hartree-Fock method.

To be concrete, we have to solve the Hartree-Fock equations (6.3.11) with the effective potential given by Eqs. (6.3.12) to (6.3.14) but without the ionic potential entering Eq. (6.3.12). Luckily, as we will soon realize, the Hartree-Fock equations are trivially solved by the plane wave states (7.1.10) opted for in Sec. 7.1, hence,

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff,\sigma}(\mathbf{r}) \right] \chi_{\mathbf{k}\sigma}(\mathbf{r}) = \epsilon_{\mathbf{k}\sigma} \chi_{\mathbf{k}\sigma}(\mathbf{r}) \quad (7.3.1)$$

holds to be true. Here the effective potential comprises besides the Hartree and the exchange potential the constant contribution arising from the ion-ion and ion-electron interaction, i.e. the second term in Eq. (7.1.22). In order to prove Eq. (7.3.1) we apply to the plane wave states the Hartree-Fock Hamiltonian comprising besides the kinetic energy the effective potential (6.3.12). Obviously, these states are eigenstates of the Laplacian,

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2 \chi_{\mathbf{k}\sigma}(\mathbf{r}) &= \frac{1}{\sqrt{\Omega}} \frac{\hbar^2}{2m} \chi_{\sigma} \nabla^2 e^{i\mathbf{k}\mathbf{r}} \\ &= \frac{\hbar^2 \mathbf{k}^2}{2m} \chi_{\mathbf{k}\sigma}(\mathbf{r}) \quad . \end{aligned} \quad (7.3.2)$$

For the direct as well as the exchange term we apply the approximate forms given in the respective last lines of Eqs. (6.3.13) and (6.3.14), which are identical to the exact formulations if both operators are used in conjunction without any further approximation. We thus note for the direct term, i.e. the Hartree potential specified by Eq. (6.3.13),

$$\begin{aligned} v_H(\mathbf{r}) \chi_{\mathbf{k}\sigma}(\mathbf{r}) &= \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r}' \frac{\rho}{|\mathbf{r} - \mathbf{r}'|} \frac{1}{\sqrt{\Omega}} \chi_{\sigma} e^{i\mathbf{k}\mathbf{r}} \\ &= \frac{e^2}{4\pi\epsilon_0} \rho \chi_{\mathbf{k}\sigma}(\mathbf{r}) \int d^3\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{N}{\Omega} \frac{e^2}{4\pi\epsilon_0} v_0(\mathbf{q} = \mathbf{0}) \chi_{\mathbf{k}\sigma}(\mathbf{r}) \quad , \end{aligned} \quad (7.3.3)$$

where we have used the identity (7.1.5). According to Eq. (6.1.21) the Hartree potential gives rise to an total energy contribution of

$$\begin{aligned}
 E_H &= \frac{1}{2} \int d^3\mathbf{r} \rho v_H(\mathbf{r}) \\
 &= \frac{1}{2} \frac{N}{\Omega} \frac{e^2}{4\pi\epsilon_0} v_0(\mathbf{q}=\mathbf{0}) \int d^3\mathbf{r} \rho \\
 &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \frac{N^2}{\Omega} \frac{4\pi}{\alpha^2} .
 \end{aligned} \tag{7.3.4}$$

As expected from our perturbation theoretical treatment adopted in Sec. 7.2 the direct term cancels exactly the constant external potential contribution arising from the combined ion-ion and ion-electron interactions. We are thus again left with only the exchange term, for which we write using Eq. (6.3.14)

$$\begin{aligned}
 v_{x,\sigma}(\mathbf{r})\chi_{\mathbf{k}\sigma}(\mathbf{r}) &= -\frac{e^2}{4\pi\epsilon_0} \sum_{\sigma'} \delta_{\sigma\sigma'} \int d^3\mathbf{r}' \frac{\rho_{\sigma\sigma'}(\mathbf{r};\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \chi_{\mathbf{k}\sigma'}(\mathbf{r}') \\
 &= -\frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}'\sigma'}^{\text{occ}} \delta_{\sigma\sigma'} \int d^3\mathbf{r}' \frac{\chi_{\mathbf{k}'\sigma'}^*(\mathbf{r}')\chi_{\mathbf{k}'\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \chi_{\mathbf{k}\sigma'}(\mathbf{r}') \\
 &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{(\Omega)^{3/2}} \sum_{\mathbf{k}'\sigma'}^{\text{occ}} \delta_{\sigma\sigma'} \chi_{\sigma'}^* \chi_{\sigma} \chi_{\sigma'} \int d^3\mathbf{r}' \frac{e^{i\mathbf{k}'(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|} e^{i\mathbf{k}\mathbf{r}'} \\
 &= -\frac{e^2}{4\pi\epsilon_0} \frac{1}{(\Omega)^{3/2}} \sum_{\mathbf{k}'\sigma'}^{\text{occ}} \delta_{\sigma\sigma'} \chi_{\sigma} \int d^3\mathbf{r}' \frac{e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|} e^{i\mathbf{k}\mathbf{r}'} \\
 &= -\frac{1}{\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}'\sigma'}^{\text{occ}} \delta_{\sigma\sigma'} v_0(\mathbf{k}-\mathbf{k}') \chi_{\mathbf{k}\sigma}(\mathbf{r}) ,
 \end{aligned} \tag{7.3.5}$$

where again we employed Eq. (7.1.5). As a result, the plane wave basis states (7.1.10) do indeed trivially solve the Hartree-Fock equations (7.3.1) with the eigenenergies specified by

$$\epsilon_{\mathbf{k}\sigma} = \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{1}{\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}'\sigma'}^{\text{occ}} \delta_{\sigma\sigma'} v_0(\mathbf{k}-\mathbf{k}') . \tag{7.3.6}$$

In this context the term “trivial” refers to the gratifying fact that solving the Hartree-Fock equations could be achieved without the need for the iterative or self-consistent field procedure, which fact is actually a consequence of the simplifications coming with the Jellium model. The resulting exact treatment within the Hartree-Fock method underlines the importance of the homogeneous electron gas for other more general schemes as e.g. the local density approximation.

At this point it also important to note that the plane waves always fulfil the Hartree-Fock equations irrespective of the actual filling of these states. In other words, from solving the Hartree-Fock equations alone we can not yet

decide, if a plane wave state with a particular wave vector \mathbf{k} and spin σ is filled or empty. Eventually, the actual occupation of the single particle states follows solely from the minimization of the total energy functional. A possible distribution arises for fixed numbers N_σ of electrons with spin σ from filling two Fermi spheres with Fermi vector $k_{F\sigma}$ for each spin. Since the Fourier transform $v_0(\mathbf{q})$ of the electron-electron interaction is a monotonically decreasing function of $|\mathbf{q}|$ this distribution does indeed minimize the total energy functional, since it i) minimizes the positive total kinetic energy and ii) maximizes the absolute value of the negative exchange energy.

According to our considerations for the Sommerfeld model in Sec. 3.1 the spin dependent Fermi wave vector is related to the spin dependent particle number by

$$\frac{4\pi k_{F\sigma}^3}{3} = N_\sigma \Omega_{\mathbf{k}} = \frac{N_\sigma (2\pi)^3}{\Omega} \quad , \quad (7.3.7)$$

which is the analogue of Eq. (3.1.5). In accordance with Eq. (3.1.6) we then note for the spin dependent electron densities

$$\rho_\sigma = \frac{N_\sigma}{\Omega} = \frac{k_{F\sigma}^3}{6\pi^2} \quad . \quad (7.3.8)$$

Of course, in the case of spin degeneracy, $N_\uparrow = N_\downarrow = \frac{N}{2}$, the spin dependent quantities are related by

$$k_{F\uparrow} = k_{F\downarrow} = k_F \quad (7.3.9)$$

and

$$\rho_\uparrow = \rho_\downarrow = \frac{k_F^3}{6\pi^2} \quad . \quad (7.3.10)$$

An alternative representation arises from expressing the spin dependent quantities in terms of the total density

$$\rho = \sum_\sigma \rho_\sigma \quad (7.3.11)$$

and the spin polarization

$$\xi = \frac{\rho_\uparrow - \rho_\downarrow}{\rho} \quad . \quad (7.3.12)$$

While $\xi = 0$ corresponds to the spin degenerate case, $\xi = 1$ refers to a totally polarized, ferromagnetic system. Writing the spin dependent densities as functions of the density and spin polarization,

$$\rho_\sigma = \frac{\rho}{2} (1 + z_\sigma \xi) \quad , \quad (7.3.13)$$

with z_σ given by Eq. (5.7.9), we are able to note for the spin dependent Fermi wave vector

$$k_{F\sigma} = (3\pi^2 \rho)^{\frac{1}{3}} \cdot (1 + z_\sigma \xi)^{\frac{1}{3}} = k_F \cdot (1 + z_\sigma \xi)^{\frac{1}{3}} \quad . \quad (7.3.14)$$

Given the spin dependent Fermi wave vectors $k_{F\sigma}$ we may now further evaluate Eq. (7.3.6) for the eigenenergies by turning the sum over the occupied states into an integral over the spin dependent Fermi sphere. However, we will use from the very beginning instead of the bare Coulomb potential the screened Coulomb potential with a finite screening parameter α . Following Eq. (2.7.2) and inserting the identity (2.6.7) we thus note

$$\begin{aligned} \sum_{\mathbf{k}'\sigma'}^{occ} \delta_{\sigma\sigma'} v_\alpha(\mathbf{k} - \mathbf{k}') &= \frac{4\pi}{\Omega_{\mathbf{k}}} \int_{\Omega_{F\sigma}} d^3\mathbf{k}' \frac{1}{(\mathbf{k} - \mathbf{k}')^2 + \alpha^2} \\ &= \frac{\Omega}{2\pi^2} \int_{\Omega_{F\sigma}} d^3\mathbf{k}' \frac{1}{(\mathbf{k} - \mathbf{k}')^2 + \alpha^2} \quad , \quad (7.3.15) \end{aligned}$$

where $\Omega_{F\sigma}$ denotes the region of the spin dependent Fermi sphere. Using spherical coordinates with the z axis parallel to the vector \mathbf{k} , the abbreviations $k = |\mathbf{k}|$ and $k' = |\mathbf{k}'|$ as well as the identity

$$(\mathbf{k} - \mathbf{k}')^2 = k^2 + (k')^2 - 2kk' \cos \vartheta \quad , \quad (7.3.16)$$

where ϑ is the angle between \mathbf{k} and \mathbf{k}' , we calculate

$$\begin{aligned} &\sum_{\mathbf{k}'\sigma'}^{occ} \delta_{\sigma\sigma'} v_\alpha(\mathbf{k} - \mathbf{k}') \\ &= \frac{\Omega}{2\pi^2} \int_0^{k_{F\sigma}} dk' (k')^2 \int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \frac{\sin \vartheta}{k^2 + (k')^2 - 2kk' \cos \vartheta + \alpha^2} \\ &= \frac{\Omega}{\pi} \int_0^{k_{F\sigma}} dk' (k')^2 \int_{-1}^1 d \cos \vartheta \frac{1}{k^2 + (k')^2 - 2kk' \cos \vartheta + \alpha^2} \\ &= \frac{\Omega}{\pi} \int_0^{k_{F\sigma}} dk' (k')^2 \left[\frac{1}{2kk'} \ln(k^2 + (k')^2 - 2kk'x + \alpha^2) \right]_1^{-1} \\ &= \frac{\Omega}{2\pi} k \int_0^{y_{F\sigma}} dy y \left[\ln((1+y)^2 + y_\alpha^2) - \ln((1-y)^2 + y_\alpha^2) \right] \quad , \quad (7.3.17) \end{aligned}$$

where we have defined

$$y = \frac{k'}{k} \quad , \quad dy = \frac{dk'}{k} \quad , \quad y_{F\sigma} = \frac{k_{F\sigma}}{k} \quad , \quad \text{and} \quad y_\alpha = \frac{\alpha}{k} \quad . \quad (7.3.18)$$

Integrating by parts we get for the integral

$$\begin{aligned} &\int_0^{y_{F\sigma}} dy y \left[\ln((1+y)^2 + y_\alpha^2) - \ln((1-y)^2 + y_\alpha^2) \right] \\ &= \frac{1}{2} \left[y^2 \ln \left(\frac{(1+y)^2 + y_\alpha^2}{(1-y)^2 + y_\alpha^2} \right) \right]_0^{y_{F\sigma}} \\ &\quad - \int_0^{y_{F\sigma}} dy y^2 \left[\frac{1+y}{(1+y)^2 + y_\alpha^2} + \frac{1-y}{(1-y)^2 + y_\alpha^2} \right] \quad . \quad (7.3.19) \end{aligned}$$

Next we split the last integral into two and substitute

$$\begin{aligned} x &= 1 + y \quad , \quad dx = dy \quad , \quad x - 1 = y \quad , \quad \text{and} \\ x &= 1 - y \quad , \quad dx = -dy \quad , \quad x - 1 = -y \quad , \end{aligned} \quad (7.3.20)$$

in the first and second integral, respectively. This leads to the result

$$\begin{aligned} & \int_0^{y_{F\sigma}} dy y \left[\ln((1+y)^2 + y_\alpha^2) - \ln((1-y)^2 + y_\alpha^2) \right] \\ &= \frac{1}{2} y_{F\sigma}^2 \ln \left(\frac{(1+y_{F\sigma})^2 + y_\alpha^2}{(1-y_{F\sigma})^2 + y_\alpha^2} \right) \\ & \quad - \int_1^{1+y_{F\sigma}} dx (x-1)^2 \frac{x}{x^2 + y_\alpha^2} + \int_1^{1-y_{F\sigma}} dx (x-1)^2 \frac{x}{x^2 + y_\alpha^2} \\ &= \frac{1}{2} y_{F\sigma}^2 \ln \left(\frac{(1+y_{F\sigma})^2 + y_\alpha^2}{(1-y_{F\sigma})^2 + y_\alpha^2} \right) - \int_{1-y_{F\sigma}}^{1+y_{F\sigma}} dx \frac{x^3 - 2x^2 + x}{x^2 + y_\alpha^2} \\ &= \frac{1}{2} y_{F\sigma}^2 \ln \left(\frac{(1+y_{F\sigma})^2 + y_\alpha^2}{(1-y_{F\sigma})^2 + y_\alpha^2} \right) \\ & \quad - \left[\frac{x^2}{2} - \frac{y_\alpha^2}{2} \ln(x^2 + y_\alpha^2) - 2x - 2y_\alpha \arctan \frac{x}{y_\alpha} + \frac{1}{2} \ln(x^2 + y_\alpha^2) \right]_{1-y_{F\sigma}}^{1+y_{F\sigma}} \\ &= \frac{1}{2} y_{F\sigma}^2 \ln \left(\frac{(1+y_{F\sigma})^2 + y_\alpha^2}{(1-y_{F\sigma})^2 + y_\alpha^2} \right) - \frac{(1+y_{F\sigma})^2 - (1-y_{F\sigma})^2}{2} \\ & \quad + 4y_{F\sigma} - \frac{1}{2} (1-y_\alpha^2) \ln \left(\frac{(1+y_{F\sigma})^2 + y_\alpha^2}{(1-y_{F\sigma})^2 + y_\alpha^2} \right) \\ & \quad - 2y_\alpha \left[\arctan \frac{1+y_{F\sigma}}{y_\alpha} - \arctan \frac{1-y_{F\sigma}}{y_\alpha} \right] \\ &= 2y_{F\sigma} + \frac{1}{2} (y_{F\sigma}^2 - 1 + y_\alpha^2) \ln \left(\frac{(1+y_{F\sigma})^2 + y_\alpha^2}{(1-y_{F\sigma})^2 + y_\alpha^2} \right) \\ & \quad - 2y_\alpha \left[\arctan \frac{1+y_{F\sigma}}{y_\alpha} - \arctan \frac{1-y_{F\sigma}}{y_\alpha} \right] \quad , \end{aligned} \quad (7.3.21)$$

which for $\alpha \rightarrow 0$ reduces to

$$\begin{aligned} & \int_0^{y_{F\sigma}} dy y \left[\ln((1+y)^2) - \ln((1-y)^2) \right] \\ &= 2y_{F\sigma} + \frac{1}{2} (y_{F\sigma}^2 - 1) \ln \left(\frac{(1+y_{F\sigma})^2}{(1-y_{F\sigma})^2} \right) \\ &= 2y_{F\sigma} + (y_{F\sigma}^2 - 1) \ln \left| \frac{1+y_{F\sigma}}{1-y_{F\sigma}} \right| \quad . \end{aligned} \quad (7.3.22)$$

Inserting Eq. (7.3.21) into Eq. (7.3.17) we arrive at

$$\sum_{\mathbf{k}'\sigma'}^{occ} \delta_{\sigma\sigma'} v_\alpha(\mathbf{k} - \mathbf{k}')$$

$$\begin{aligned}
 &= \frac{\Omega}{2\pi} \left[2k_{F\sigma} + \frac{1}{2k} (k_{F\sigma}^2 - k^2 + \alpha^2) \ln \left(\frac{(k + k_{F\sigma})^2 + \alpha^2}{(k - k_{F\sigma})^2 + \alpha^2} \right) \right. \\
 &\quad \left. - 2\alpha \left[\arctan \frac{k + k_{F\sigma}}{\alpha} - \arctan \frac{k - k_{F\sigma}}{\alpha} \right] \right] , \tag{7.3.23}
 \end{aligned}$$

and, finally combining this with the relation (7.3.6) for the eigenenergies as generalized for arbitrary values of α , we obtain the result

$$\begin{aligned}
 \epsilon_{\mathbf{k}\sigma} &= \frac{\hbar^2 \mathbf{k}^2}{2m} \\
 &\quad - \frac{k_{F\sigma}}{2\pi} \frac{e^2}{4\pi\epsilon_0} \left[2 + \frac{k_{F\sigma}^2 - k^2 + \alpha^2}{2kk_{F\sigma}} \ln \left(\frac{(k + k_{F\sigma})^2 + \alpha^2}{(k - k_{F\sigma})^2 + \alpha^2} \right) \right. \\
 &\quad \left. - 2 \frac{\alpha}{k_{F\sigma}} \left[\arctan \frac{k + k_{F\sigma}}{\alpha} - \arctan \frac{k - k_{F\sigma}}{\alpha} \right] \right] \\
 &= \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{k_{F\sigma}}{2\pi} \frac{e^2}{4\pi\epsilon_0} G \left(\frac{k}{k_{F\sigma}}, \frac{\alpha}{k_{F\sigma}} \right) , \tag{7.3.24}
 \end{aligned}$$

where, in the last step, we have defined the function

$$\begin{aligned}
 G(x, z) &= 2 + \frac{1 - x^2 + z^2}{2x} \ln \left(\frac{(x + 1)^2 + z^2}{(x - 1)^2 + z^2} \right) \\
 &\quad - 2z \left[\arctan \frac{x + 1}{z} - \arctan \frac{x - 1}{z} \right] . \tag{7.3.25}
 \end{aligned}$$

Again we note explicitly the results for the case $\alpha \rightarrow 0$,

$$\begin{aligned}
 \epsilon_{\mathbf{k}\sigma} &= \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{k_{F\sigma}}{2\pi} \frac{e^2}{4\pi\epsilon_0} \left[2 + \frac{k_{F\sigma}^2 - k^2}{kk_{F\sigma}} \ln \left| \frac{k + k_{F\sigma}}{k - k_{F\sigma}} \right| \right] \\
 &= \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{k_{F\sigma}}{2\pi} \frac{e^2}{4\pi\epsilon_0} F \left(\frac{k}{k_{F\sigma}} \right) , \tag{7.3.26}
 \end{aligned}$$

where we have introduced the function

$$F(x) = G(x, z = 0) = 2 + \frac{1 - x^2}{x} \ln \left| \frac{1 + x}{1 - x} \right| , \tag{7.3.27}$$

shown in Fig. 7.3. Note, in particular, the logarithmic divergence of its derivative at $x = 1$, hence, at $k = k_{F\sigma}$, which is transferred to our result for the single particle energies. It appears for $\mathbf{k} = \mathbf{k}'$ and, hence, can be traced back to the divergence of the Fourier transform (7.1.5) of the Coulombic electron-electron interaction at $\mathbf{q} = \mathbf{0}$. This becomes obvious from a plot of the function $G(x, z)$ given in Fig. 7.4. While for $\alpha = 0$ (foremost curve) we recognize the function $F(k/k_{F\sigma})$, the logarithmic divergence of the derivative vanishes as soon as α

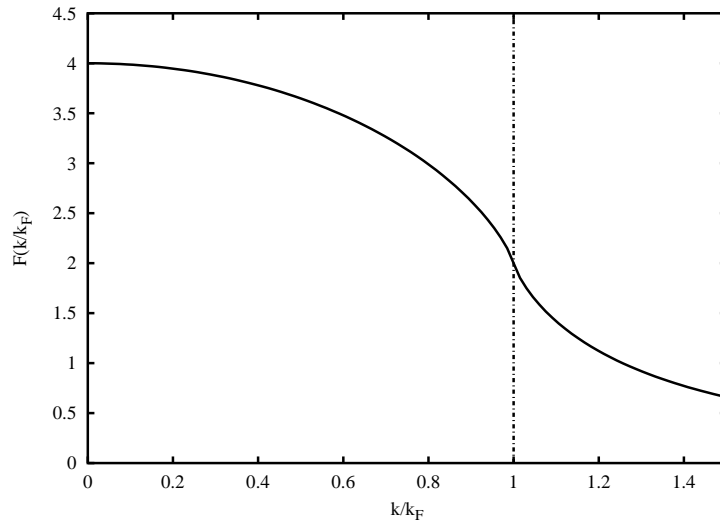


Figure 7.3: Function $F(k/k_{F\sigma})$ as defined by Eq. (7.3.27).

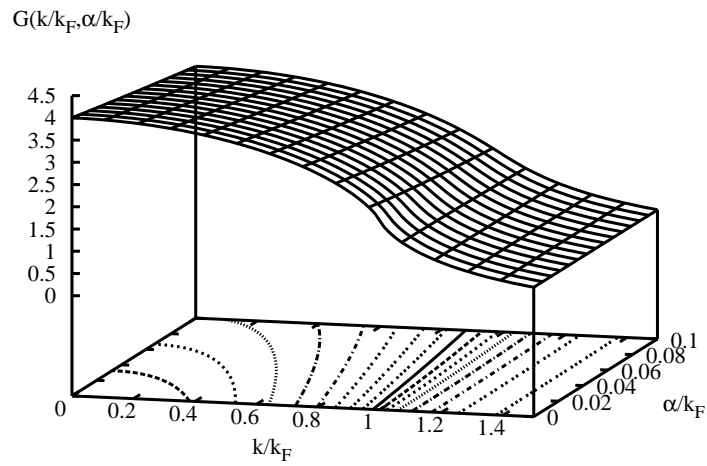


Figure 7.4: Function $G(k/k_{F\sigma}, \alpha/k_{F\sigma})$ as defined by Eq. (7.3.25).

deviates from zero. To conclude, the divergence of $dF(x)/dx$ is just an artefact of the neglect of screening in the Hartree-Fock treatment of the homogeneous electron gas. It causes, in addition, a vanishing density of states at the Fermi

energy since the gradient of the single particle energies diverges logarithmically at the Fermi energy,

$$\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}\sigma} \Big|_{\epsilon_{\mathbf{k}\sigma}=E_{F\sigma}} \rightarrow \infty, \quad (7.3.28)$$

and, according to Eq. (2.7.13), the density of states at E_F goes to zero.

In order to visualize the eigenenergies it is useful to scale them by the spin dependent Fermi energy,

$$E_{F\sigma} = \frac{\hbar^2 k_{F\sigma}^2}{2m}. \quad (7.3.29)$$

With the help of the definition (3.1.10) of the Bohr radius and the relation (3.1.9) of the Fermi wave vector to a likewise spin dependent density parameter $r_{s\sigma}$ we thus write

$$\begin{aligned} \frac{\epsilon_{\mathbf{k}\sigma}}{E_{F\sigma}} &= \frac{\mathbf{k}^2}{k_{F\sigma}^2} - \frac{2m}{2\pi\hbar^2 k_{F\sigma}} \frac{e^2}{4\pi\epsilon_0} G\left(\frac{k}{k_{F\sigma}}, \frac{\alpha}{k_{F\sigma}}\right) \\ &= \frac{\mathbf{k}^2}{k_{F\sigma}^2} - \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{\pi} \frac{r_{s\sigma}}{a_B} G\left(\frac{k}{k_{F\sigma}}, \frac{\alpha}{k_{F\sigma}}\right) \\ &= \frac{\mathbf{k}^2}{k_{F\sigma}^2} - 0.166 \frac{r_{s\sigma}}{a_B} G\left(\frac{k}{k_{F\sigma}}, \frac{\alpha}{k_{F\sigma}}\right). \end{aligned} \quad (7.3.30)$$

For $\alpha = 0$ as well as $\alpha = 0.02k_{F\sigma}$ and a typical value of the density parameter, $r_{s\sigma}/a_B = 4$, these scaled eigenenergies are displayed in Fig. 7.5, where we

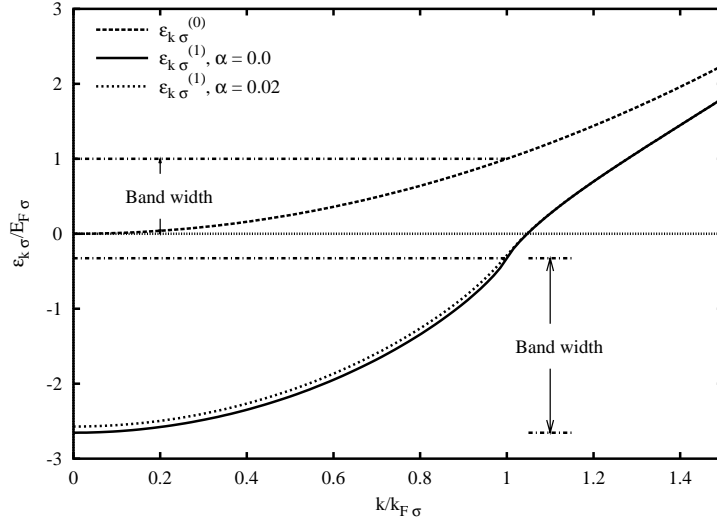


Figure 7.5: Spin dependent eigenenergies $\epsilon_{\mathbf{k}\sigma}$ of the homogeneous electron gas scaled to the spin dependent Fermi energy $E_{F\sigma}$.

have added the free electron dispersion curve (3.1.4). Obviously, in addition to substantially lowering the electronic single particle energies the exchange

term causes a considerable increase of the occupied band width by a factor of $1 + 0.332r_{s\sigma}/a_B$, hence, in our case by 2.327. This effect, however, has not been observed in photoelectron spectroscopy experiments. Introducing a finite but small value of α has the effect of removing the logarithmic divergence of the derivative of the single particle energies with respect to $|\mathbf{k}|$, as was already observed in the discussion of the functions $F(x)$ and $G(x, z)$ above. Yet, it does not cure the afore mentioned discrepancy between theory and experiment as long as α is kept at reasonable, hence, small values.

Finally, we point to the important fact that, on inclusion of the exchange term, only the single particle energies change from the free electron dispersion to the expression (7.3.24)/(7.3.26) while the single particle states remain to be plane waves.

With the single particle energies $\epsilon_{\mathbf{k}\sigma}$ at hand we may now calculate the total ground state energy, which, within Hartree-Fock theory, reads according to Eq. (6.1.22) as the sum of all single particle energies minus the double counting term

$$\langle H_0 \rangle = \sum_{\mathbf{k}\sigma}^{\text{occ}} \epsilon_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\mathbf{k}\sigma}^{\text{occ}} \sum_{\mathbf{k}'\sigma'}^{\text{occ}} A_{\mathbf{k}\sigma, \mathbf{k}'\sigma'} \quad , \quad (7.3.31)$$

where we still relied on the approximate forms of the direct and exchange term and thus allowed for formal inclusion of the self-interaction term. For the plane wave basis set the exchange integral assumes the form

$$\begin{aligned} A_{\mathbf{k}\sigma, \mathbf{k}'\sigma'} &= \frac{e^2}{4\pi\epsilon_0} \delta_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\chi_{\mathbf{k}\sigma}^*(\mathbf{r}) \chi_{\mathbf{k}'\sigma'}^*(\mathbf{r}') \chi_{\mathbf{k}\sigma'}(\mathbf{r}') \chi_{\mathbf{k}\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{\Omega^2} \delta_{\sigma\sigma'} \chi_{\sigma}^* \chi_{\sigma'}^* \chi_{\sigma'} \chi_{\sigma} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{e^{-i(\mathbf{k}-\mathbf{k}') \cdot (\mathbf{r}-\mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} \\ &= \frac{e^2}{4\pi\epsilon_0} \frac{1}{\Omega} \delta_{\sigma\sigma'} v_0(\mathbf{k} - \mathbf{k}') \quad , \end{aligned} \quad (7.3.32)$$

Inserting this into the ground state energy (7.3.31) and using Eq. (7.3.6) for the single particle energies we obtain the result

$$\begin{aligned} \langle H_0 \rangle &= \sum_{\mathbf{k}\sigma}^{\text{occ}} \epsilon_{\mathbf{k}\sigma} + \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}\sigma}^{\text{occ}} \sum_{\mathbf{k}'\sigma'}^{\text{occ}} \delta_{\sigma\sigma'} v_{\alpha}(\mathbf{k} - \mathbf{k}') \\ &= \sum_{\mathbf{k}\sigma}^{\text{occ}} \frac{\hbar^2 \mathbf{k}^2}{2m} - \frac{1}{2\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}\sigma}^{\text{occ}} \sum_{\mathbf{k}'\sigma'}^{\text{occ}} \delta_{\sigma\sigma'} v_{\alpha}(\mathbf{k} - \mathbf{k}') \quad . \end{aligned} \quad (7.3.33)$$

Two points need to be mentioned in this context: First, we have replaced in Eq. (7.3.33) the bare Coulomb potential $v_0(\mathbf{q})$ by its screened counterpart $v_{\alpha}(\mathbf{q})$ in order to account for the logarithmic divergence of the derivative of the single particle energies at $k = k_{F\sigma}$. Second, on comparing the expression (7.3.33) to the perturbation theoretical treatment followed in Sec. 7.2, specifically, to the first order energy correction (7.2.3), we realize that both approaches yield completely identical results. We may thus, in general, identify Hartree-Fock

theory with first order perturbation theory and, as a consequence, adopt the final expression (7.2.11) as well as discussion following Fig. 7.1.

Nevertheless, it is instructive to proceed in a slightly different way here and to include the effect of a finite spin polarization. To this end we calculate the first contribution to Eq. (7.3.27) as

$$\begin{aligned}
 \frac{E_0}{N} &= \frac{1}{N} \sum_{\mathbf{k}\sigma}^{occ} \frac{\hbar^2 \mathbf{k}^2}{2m} \\
 &= \frac{\Omega}{(2\pi)^3 N} \frac{\hbar^2}{2m} \sum_{\sigma} \int_{\Omega_{F\sigma}} d^3\mathbf{k} \mathbf{k}^2 \\
 &= \frac{\Omega}{2\pi^2 N} \frac{\hbar^2}{2m} \sum_{\sigma} \int_0^{k_{F\sigma}} dk k^4 \\
 &= \frac{1}{5} \frac{\Omega}{2\pi^2 N} \frac{\hbar^2}{2m} \sum_{\sigma} k_{F\sigma}^5 \\
 &= \frac{1}{5} \frac{\Omega}{2\pi^2 N} \frac{\hbar^2}{2m} k_F^2 3\pi^3 \rho \sum_{\sigma} (1 + z_{\sigma}\xi)^{\frac{5}{3}} \\
 &= \frac{3}{5} E_F \cdot \frac{1}{2} \sum_{\sigma} (1 + z_{\sigma}\xi)^{\frac{5}{3}} \quad . \quad (7.3.34)
 \end{aligned}$$

Here we have used the identities (2.7.2), (2.6.7), (3.1.6), (3.1.7), (3.1.11), and (7.3.14). Obviously, for zero spin polarization Eq. (7.3.34) reduces to the result (3.1.18) for the Sommerfeld model.

For the exchange contribution to the ground state energy we combine Eqs. (7.3.14) and (7.3.32) and note

$$\begin{aligned}
 \frac{\Delta E^{(1)}}{N} &= -\frac{1}{2N\Omega} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}\sigma}^{occ} \sum_{\mathbf{k}'\sigma'}^{occ} \delta_{\sigma\sigma'} v_{\alpha}(\mathbf{k} - \mathbf{k}') \\
 &= -\frac{1}{2N} \frac{1}{2\pi} \frac{e^2}{4\pi\epsilon_0} \sum_{\mathbf{k}\sigma}^{occ} k_{F\sigma} \delta_{\sigma\sigma'} G\left(\frac{k}{k_{F\sigma'}}, \frac{\alpha}{k_{F\sigma'}}\right) \\
 &= -\frac{\Omega}{2N} \frac{1}{(2\pi)^3} \frac{1}{2\pi} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma} k_{F\sigma} \int_{\Omega_{F\sigma}} d^3\mathbf{k} G\left(\frac{k}{k_{F\sigma}}, \frac{\alpha}{k_{F\sigma}}\right) \\
 &= -\frac{\Omega}{2N} \frac{1}{(2\pi)^3} \frac{1}{2\pi} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma} 4\pi k_{F\sigma}^4 \int_0^1 dy y^2 G(y, y_{\alpha}) \quad . \quad (7.3.35)
 \end{aligned}$$

In order to facilitate interpretation of the final results it is instructive to treat the case $\alpha = 0$ separately. We thus replace in Eq. (7.3.35) the function $G(y, y_{\alpha})$ by $F(y)$,

$$\frac{\Delta E^{(1)}}{N} = -\frac{\Omega}{2N} \frac{1}{(2\pi)^3} \frac{1}{2\pi} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma} 4\pi k_{F\sigma}^4 \int_0^1 dy y^2 F(y) \quad , \quad (7.3.36)$$

and calculate the integral as

$$\begin{aligned}
& \int_0^1 dy y^2 F(y) \\
&= \int_0^1 dy y^2 \left[2 + \frac{1-y^2}{y} \ln \left| \frac{1+y}{1-y} \right| \right] \\
&= \frac{2}{3} + \int_0^1 dy y(1-y^2) \ln \left| \frac{1+y}{1-y} \right| \\
&= \frac{2}{3} + \left(-\frac{1}{4} \right) \left[(1-y^2)^2 \ln \left| \frac{1+y}{1-y} \right| \right]_0^1 \\
&\quad - \left(-\frac{1}{4} \right) \int_0^1 dy (1-y^2)^2 \left[\frac{1}{1+y} + \frac{1}{1-y} \right] \\
&= \frac{2}{3} + \frac{1}{2} \int_0^1 dy (1-y^2) \\
&= 1 \quad , \tag{7.3.37}
\end{aligned}$$

which leads to the intermediate result

$$\int_{\Omega_{F\sigma}} d^3\mathbf{k} F\left(\frac{k}{k_{F\sigma'}}\right) = 4\pi k_{F\sigma}^3 \quad . \tag{7.3.38}$$

In contrast, for $\alpha \neq 0$ the integral entering Eq. (7.3.35) is evaluated as

$$\begin{aligned}
& \int_0^1 dy y^2 G(y, y_\alpha) \\
&= \int_0^1 dy y^2 \left[2 + \frac{1-y^2+y_\alpha^2}{2y} \ln \left(\frac{(1+y)^2+y_\alpha^2}{(1-y)^2+y_\alpha^2} \right) \right. \\
&\quad \left. - 2y_\alpha \left[\arctan \frac{1+y}{y_\alpha} + \arctan \frac{1-y}{y_\alpha} \right] \right] \\
&= \frac{2}{3} + \left(-\frac{1}{8} \right) \left[(1-y^2+y_\alpha^2)^2 \ln \left(\frac{(1+y)^2+y_\alpha^2}{(1-y)^2+y_\alpha^2} \right) \right]_0^1 \\
&\quad - \left(-\frac{1}{4} \right) \int_0^1 dy \left((1+y)(1-y) + y_\alpha^2 \right)^2 \\
&\quad \quad \quad \left[\frac{1+y}{(1+y)^2+y_\alpha^2} + \frac{1-y}{(1-y)^2+y_\alpha^2} \right] \\
&\quad - 2y_\alpha \int_0^1 dy y^2 \left[\arctan \frac{1+y}{y_\alpha} + \arctan \frac{1-y}{y_\alpha} \right] \quad . \tag{7.3.39}
\end{aligned}$$

As before, we apply the substitutions (7.3.20) in the first and second integral, respectively, of the second but last line and note

$$\int_0^1 dy y^2 G(y, y_\alpha)$$

$$\begin{aligned}
 &= \frac{2}{3} - \frac{1}{8}y_\alpha^4 \ln\left(\frac{4+y_\alpha^2}{y_\alpha^2}\right) + \frac{1}{4} \int_0^2 dx (x(2-x) + y_\alpha^2)^2 \frac{x}{x^2 + y_\alpha^2} \\
 &\quad - 2y_\alpha \int_0^2 dx (x-1)^2 \arctan \frac{x}{y_\alpha} . \quad (7.3.40)
 \end{aligned}$$

In order to evaluate the second integral we note the identities

$$x(2-x) + y_\alpha^2 = -(x^2 + y_\alpha^2) + 2(x + y_\alpha^2) , \quad (7.3.41)$$

$$\begin{aligned}
 \frac{x(2-x) + y_\alpha^2}{x^2 + y_\alpha^2} &= -x + 2 \frac{x^2 + xy_\alpha^2}{x^2 + y_\alpha^2} \\
 &= 2 - x + 2y_\alpha^2 \frac{x-1}{x^2 + y_\alpha^2} , \quad (7.3.42)
 \end{aligned}$$

and

$$\begin{aligned}
 &(x(2-x) + y_\alpha^2)^2 \frac{x}{x^2 + y_\alpha^2} \\
 &= x(2-x)^2 + (2-x)y_\alpha^2 - 2y_\alpha^2(x-1) + 4y_\alpha^2 \frac{x-1}{x^2 + y_\alpha^2}(x + y_\alpha^2) \\
 &= x^3 - 4x^2 + 4x + 4y_\alpha^2 - 3xy_\alpha^2 + 4y_\alpha^2 \frac{x^2 + y_\alpha^2 - y_\alpha^2 - x + xy_\alpha^2 - y_\alpha^2}{x^2 + y_\alpha^2} \\
 &= x^3 - 4x^2 + (4 - 3y_\alpha^2)x + 8y_\alpha^2 + 4y_\alpha^2(y_\alpha^2 - 1) \frac{x}{x^2 + y_\alpha^2} - 8y_\alpha^4 \frac{1}{x^2 + y_\alpha^2} \\
 &\quad . \quad (7.3.43)
 \end{aligned}$$

Inserting this into Eq. (7.3.40) we get

$$\begin{aligned}
 &\int_0^1 dy y^2 G(y, y_\alpha) \\
 &= \frac{2}{3} - \frac{1}{8}y_\alpha^4 \ln\left(\frac{4+y_\alpha^2}{y_\alpha^2}\right) + \frac{1}{3} + \frac{5}{2}y_\alpha^2 \\
 &\quad + \left[\frac{1}{2}y_\alpha^2(y_\alpha^2 - 1) \ln(x^2 + y_\alpha^2) - 2y_\alpha^3 \arctan \frac{x}{y_\alpha} \right]_0^2 \\
 &\quad - 2y_\alpha \left[\frac{x^3}{3} \arctan \frac{x}{y_\alpha} - \frac{y_\alpha x^2}{6} + \frac{y_\alpha^3}{6} \ln(x^2 + y_\alpha^2) \right. \\
 &\quad \quad \left. - (x^2 + y_\alpha^2) \arctan \frac{x}{y_\alpha} + xy_\alpha + x \arctan \frac{x}{y_\alpha} \right. \\
 &\quad \quad \left. - \frac{y_\alpha}{2} \ln(x^2 + y_\alpha^2) \right]_0^2 \\
 &= 1 - \frac{1}{6}y_\alpha^2 + y_\alpha^2 \left(\frac{1}{2} + \frac{y_\alpha^2}{24} \right) \ln\left(\frac{4+y_\alpha^2}{y_\alpha^2}\right) - \frac{4}{3}y_\alpha \arctan \frac{2}{y_\alpha} \\
 &= 1 - \frac{4}{3}y_\alpha \arctan \frac{2}{y_\alpha} - \frac{y_\alpha^2}{6} \left[1 - \left(\frac{y_\alpha^2}{4} + 3 \right) \ln\left(1 + \frac{4}{y_\alpha^2}\right) \right] . \quad (7.3.44)
 \end{aligned}$$

Defining a screening function

$$H(z) = 1 - \frac{4}{3}z \arctan \frac{2}{z} - \frac{z^2}{6} \left[1 - \left(\frac{z^2}{4} + 3 \right) \ln \left(1 + \frac{4}{z^2} \right) \right] , \quad (7.3.45)$$

which is displayed in Fig. 7.6, we are able to write the previous expression as

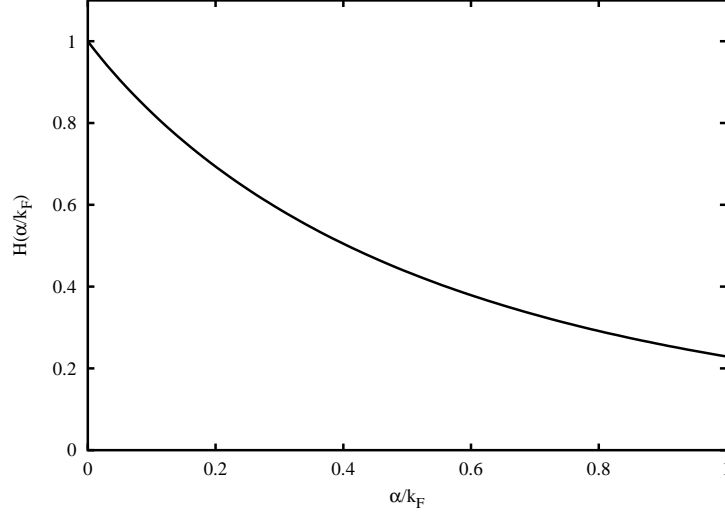


Figure 7.6: Screening function $H(\alpha/k_F)$ entering Eq. (7.3.45).

$$\int_{\Omega_{F\sigma}} d^3\mathbf{k} G\left(\frac{k}{k_{F\sigma}}, \frac{\alpha}{k_{F\sigma}}\right) = 4\pi k_{F\sigma}^3 \cdot H\left(\frac{\alpha}{k_{F\sigma}}\right) . \quad (7.3.46)$$

Finally, inserting this into Eq. (7.3.35) we write the first order energy correction per particle as

$$\begin{aligned} \frac{\Delta E^{(1)}}{N} &= -\frac{\Omega}{N} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma} \frac{k_{F\sigma}^4}{(2\pi)^3} \cdot H\left(\frac{\alpha}{k_{F\sigma}}\right) \\ &= -\frac{\Omega}{N} \frac{e^2}{4\pi\epsilon_0} \frac{k_F^4}{4\pi^3} \frac{1}{2} \sum_{\sigma} (1 + z_{\sigma}\xi)^{\frac{4}{3}} \cdot H\left(\frac{\alpha}{k_{F\sigma}}\right) \\ &= -\frac{e^2}{4\pi\epsilon_0} \frac{3}{4\pi} k_F \frac{1}{2} \sum_{\sigma} (1 + z_{\sigma}\xi)^{\frac{4}{3}} \cdot H\left(\frac{\alpha}{k_{F\sigma}}\right) . \quad (7.3.47) \end{aligned}$$

Summarizing we thus obtain for the total ground state energy per particle

$$\begin{aligned} \frac{\langle H_0 \rangle}{N} &= \frac{3}{5} E_F \cdot \frac{1}{2} \sum_{\sigma} (1 + z_{\sigma}\xi)^{\frac{5}{3}} \\ &\quad - \frac{e^2}{4\pi\epsilon_0} \frac{3}{4\pi} k_F \frac{1}{2} \sum_{\sigma} (1 + z_{\sigma}\xi)^{\frac{4}{3}} \cdot H\left(\frac{\alpha}{k_{F\sigma}}\right) \end{aligned}$$

$$\begin{aligned}
 &= \left[\frac{2.21}{(r_s/a_B)^2} \cdot \frac{1}{2} \sum_{\sigma} (1 + z_{\sigma}\xi)^{\frac{5}{3}} \right. \\
 &\quad \left. - \frac{0.916}{r_s/a_B} \cdot \frac{1}{2} \sum_{\sigma} (1 + z_{\sigma}\xi)^{\frac{4}{3}} \cdot H\left(\frac{\alpha}{k_{F\sigma}}\right) \right] \text{Ryd} \quad , \\
 &\hspace{15em} (7.3.48)
 \end{aligned}$$

which, as expected reduces to the ground state energy (7.2.11) of the spin degenerate case for $\xi = 0$. The present result for arbitrary values of density parameter r_s and spin polarization ξ as well as for $\alpha = 0$ is displayed in Fig. 7.7, which generalizes Fig. 7.2 and where again we have included the energy

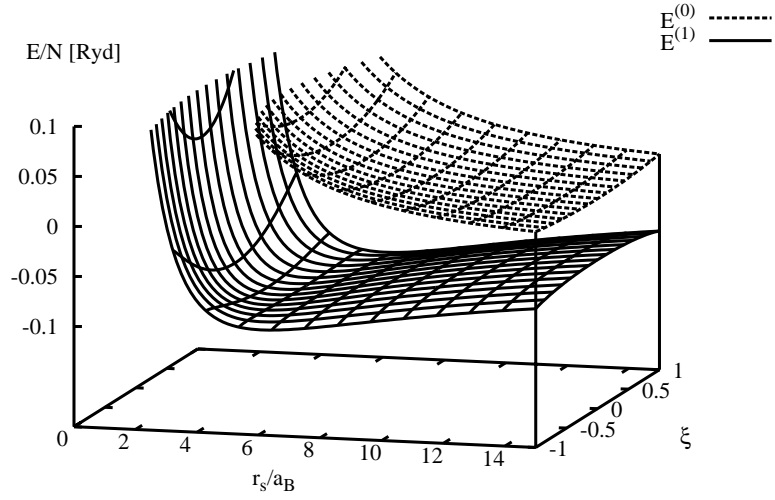


Figure 7.7: Hartree-Fock ground state energy per particle of the Jellium model as a function of density parameter r_s and spin polarization ξ ; the dotted curves (upper sheet) show the zeroth order result arising from the Sommerfeld model.

surface obtained from the Sommerfeld model. While the latter obviously leads neither to metallic binding at finite values of r_s nor to a finite spin polarization, the homogeneous electron gas does allow for both. As already outlined at the end of Sec. 7.2 the ground state has a minimum for $\xi = 0$ at $r_s = 4.83a_B$ we observe a change in curvature as a function of ξ on going from $r_s \approx 5a_B$ to higher values. As an explicit calculation reveals, the fully polarized $\xi = 1$ case becomes more stable than the spin degenerate system for $r_s > 5.45a_B$. We thus expect a phase transition to a ferromagnetic ground state for small electronic densities. However, metals with such low densities do not seem to exist and for this reason such a ferromagnetic ground state has not been observed.

7.4 The exchange hole

In Sec. 5.7 we have defined several types of electron density operators arising as combinations of electronic field operators. In particular, we had discussed the operator $\hat{P}_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')$, which gave the probability of finding an electron with spin σ at position \mathbf{x} and a second electron with spin σ' at position \mathbf{x}' . In Eq. (5.7.23) we expressed the expectation value of this operator in terms of the spin dependent electron densities as well as the corresponding density matrices as

$$P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = \rho_{\sigma}(\mathbf{x}) \cdot \rho_{\sigma'}(\mathbf{x}') - |\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')|^2 \quad . \quad (7.4.1)$$

It is very instructive to study this quantity for the homogeneous electron gas. In this case the single particle orbitals are plane waves according to Eq. (7.1.10) and the spin dependent electronic density is given by Eq. (7.3.8). In contrast, the spin dependent density matrix can be expressed via Eq. (5.7.17) in terms of the spin dependent single particle orbitals as

$$\begin{aligned} \rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') &= \sum_{\alpha}^{occ} \chi_{\alpha;\sigma'}^*(\mathbf{x}') \chi_{\alpha;\sigma}(\mathbf{x}) \\ &= \sum_{\mathbf{k}}^{occ} \frac{1}{\Omega} e^{-i\mathbf{k}\mathbf{x}'} e^{i\mathbf{k}\mathbf{x}} \chi_{\sigma'}^* \chi_{\sigma} \\ &= \frac{1}{\Omega} \frac{\Omega}{(2\pi)^3} \int d^3\mathbf{k} \Theta(k_F - |\mathbf{k}|) e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}')} \chi_{\sigma'}^* \chi_{\sigma} \\ &= \frac{1}{(2\pi)^3} \delta_{\sigma\sigma'} \int d^3\mathbf{k} \Theta(k_F - |\mathbf{k}|) e^{i\mathbf{k}(\mathbf{x}-\mathbf{x}')} \quad , \quad (7.4.2) \end{aligned}$$

where in the last step we have used the identity (2.7.2) as well as the fact that in the ground state the occupied single particle states are found within the Fermi sphere. Furthermore, the Kronecker δ with respect to the spins reflects the fact that the eigenstates are pure spin states. The integral entering Eq. (7.4.2) is readily calculated as

$$\begin{aligned} \int_{\Omega_F} d^3\mathbf{q} e^{i\mathbf{q}\mathbf{r}} &= \int_0^{k_F} dq q^2 \int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta \sin\vartheta e^{iqr \cos\vartheta} \\ &= 2\pi \int_0^{k_F} dq q^2 \int_{-1}^1 d \cos\vartheta e^{iqr \cos\vartheta} \\ &= \frac{2\pi}{ir} \int_0^{k_F} dq q (e^{iqr} - e^{-iqr}) \\ &= \frac{4\pi}{r} \int_0^{k_F} dq q \sin(qr) \\ &= \frac{4\pi}{r} \left[\frac{\sin(qr)}{r^2} - \frac{q \cos(qr)}{r} \right]_0^{k_F} \\ &= 4\pi k_F^3 \left[\frac{\sin(k_F r) - k_F r \cos(k_F r)}{(k_F r)^3} \right] \end{aligned}$$

$$= 4\pi k_F^3 \frac{j_1(k_F r)}{k_F r} . \quad (7.4.3)$$

In the last step we have used the definition of the spherical Bessel function. Inserting Eq. (7.4.3) into Eq. (7.4.2) we obtain for the spin dependent electron density matrix the result

$$\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') = \frac{1}{2\pi^2} \delta_{\sigma\sigma'} k_F^3 \frac{\sin(k_F |\mathbf{x} - \mathbf{x}'|) - k_F |\mathbf{x} - \mathbf{x}'| \cos(k_F |\mathbf{x} - \mathbf{x}'|)}{(k_F |\mathbf{x} - \mathbf{x}'|)^3} . \quad (7.4.4)$$

Combining the identities (7.4.1), (7.3.8), and (7.4.4) we finally arrive at

$$\begin{aligned} P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') &= \rho_\sigma \cdot \rho_{\sigma'} - |\rho_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')|^2 \\ &= \left(\frac{k_F^3}{6\pi^2} \right)^2 - \delta_{\sigma\sigma'} \left(\frac{k_F^3}{2\pi^2} \right)^2 \left(\frac{\sin(k_F |\mathbf{x} - \mathbf{x}'|) - k_F |\mathbf{x} - \mathbf{x}'| \cos(k_F |\mathbf{x} - \mathbf{x}'|)}{(k_F |\mathbf{x} - \mathbf{x}'|)^3} \right)^2 \\ &= \rho_\sigma \cdot \rho_{\sigma'} \left[1 - 9 \cdot \delta_{\sigma\sigma'} \left(\frac{\sin(k_F |\mathbf{x} - \mathbf{x}'|) - k_F |\mathbf{x} - \mathbf{x}'| \cos(k_F |\mathbf{x} - \mathbf{x}'|)}{(k_F |\mathbf{x} - \mathbf{x}'|)^3} \right)^2 \right] \end{aligned} \quad (7.4.5)$$

and, summing over spins, we obtain

$$\begin{aligned} \sum_{\sigma\sigma'} P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') &= \rho^2 \left[1 - \frac{9}{2} \left(\frac{\sin(k_F |\mathbf{x} - \mathbf{x}'|) - k_F |\mathbf{x} - \mathbf{x}'| \cos(k_F |\mathbf{x} - \mathbf{x}'|)}{(k_F |\mathbf{x} - \mathbf{x}'|)^3} \right)^2 \right] . \end{aligned} \quad (7.4.6)$$

Inserting this expression into the definition (5.7.31) of the spin dependent pair correlation functions and again summing over spins we thus arrive at

$$\begin{aligned} g(\mathbf{x} - \mathbf{x}') &= g(\mathbf{x}; \mathbf{x}') \\ &= \frac{1}{4} \sum_{\sigma\sigma'} g_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}') \\ &= \frac{1}{4} \sum_{\sigma\sigma'} \frac{P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')}{\rho_\sigma(\mathbf{x}) \cdot \rho_{\sigma'}(\mathbf{x}')} \\ &= \left[1 - \frac{9}{2} \left(\frac{\sin(k_F |\mathbf{x} - \mathbf{x}'|) - k_F |\mathbf{x} - \mathbf{x}'| \cos(k_F |\mathbf{x} - \mathbf{x}'|)}{(k_F |\mathbf{x} - \mathbf{x}'|)^3} \right)^2 \right] . \end{aligned} \quad (7.4.7)$$

For $\mathbf{x} = \mathbf{x}'$ the pair correlation function assumes the value $g(\mathbf{0}) = \frac{1}{2}$. This is visible from Fig. 7.8, where we display the spin summed pair correlation function as a function of $r = |\mathbf{x} - \mathbf{x}'|$. In addition, Fig. 7.9 shows the same

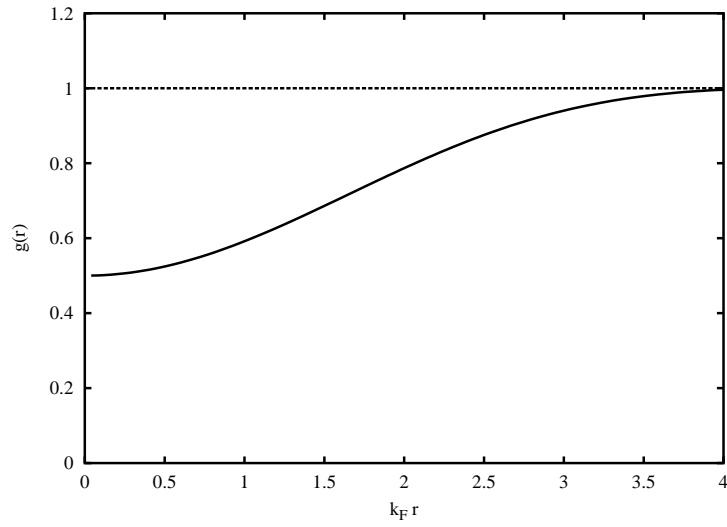


Figure 7.8: Pair correlation function $g(r)$ of the homogeneous non-interacting electron gas for small values of $k_F r$.

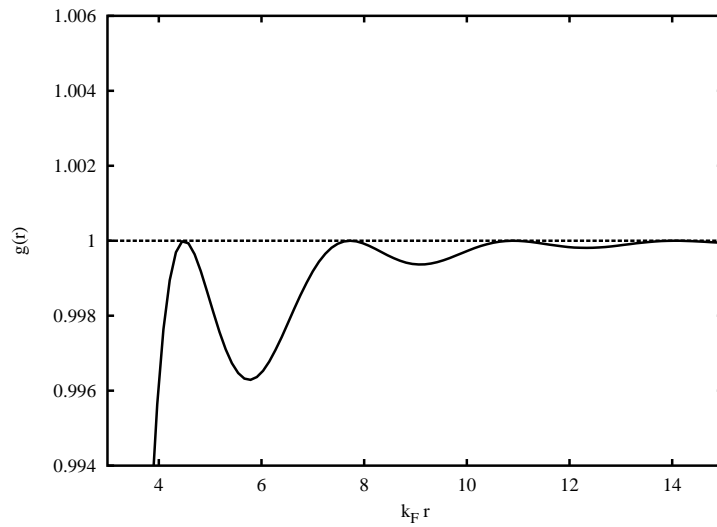


Figure 7.9: Pair correlation function $g(r)$ of the homogeneous non-interacting electron gas for large values of $k_F r$ on an expanded scale.

function for larger values of $k_F r$ on an expanded energy scale around $g(\mathbf{x} - \mathbf{x}') = 1$. The oscillations of $g(\mathbf{x} - \mathbf{x}')$ for large values of $k_F r$, which have a wavelength $\frac{\pi}{k_F}$, result from the discontinuity in the \mathbf{k} space occupation at the Fermi surface.

According to Fig. 7.8 the probability of finding a particle at \mathbf{x} and another

particle at \mathbf{x}' is considerably reduced if the particles approach each other. For zero distance r between both particles this probability drops to $\frac{1}{2}$. This particular limiting value can be traced back to the Kronecker δ with respect to spins growing out of the spin dependent density matrix (7.4.4) for pure spin states. Since the spin dependent density matrix comprises the exchange contribution to the quantity $P_{\sigma\sigma'}(\mathbf{x}; \mathbf{x}')$ the reduction of the pair correlation functions for small values of $k_F r$, which is denoted as the exchange hole, can eventually be attributed to the Pauli principle, which requires two electrons with like spin to keep at a distance. However, while electrons with equal spins are forbidden to stay at the same position, the motion of electrons with different spins is not restricted at all. In particular, in the latter case the two electrons may come arbitrarily close. This explains why the pair correlation function does not fall *below* the value of $\frac{1}{2}$. From a physical point of view, we may interpret the exchange hole as being attached to each electron. In other words, while moving through the crystal, each electron carries such an exchange hole around it. The combination of both the electron and its exchange hole thus constitutes the simplest example of a quasiparticle.

In closing this section we calculate the integral of the pair correlation function over all space. If scaled by the constant density this integral is identical to the number of electrons pushed away from the original particle due to the Pauli principle. We note

$$\begin{aligned}
 \int d^3\mathbf{x}' \rho [g(\mathbf{x} - \mathbf{x}') - 1] &= -\frac{9}{2}\rho \int d^3\mathbf{x}' \left(\frac{j_1(k_F|\mathbf{x} - \mathbf{x}'|)}{k_F|\mathbf{x} - \mathbf{x}'|} \right)^2 \\
 &= -\frac{9}{2} \frac{k_F^3}{3\pi^2} 4\pi \int_0^\infty dx x^2 \left(\frac{j_1(k_F x)}{k_F x} \right)^2 \\
 &= -\frac{6}{\pi} \int_0^\infty dz (j_1(z))^2 \quad . \quad (7.4.8)
 \end{aligned}$$

Here we have in the last step changed the integration variable from x to $z = k_F x$. In addition, we have used Eq. (3.1.7) to express the density in terms of the Fermi wave vector. The integral over the square of the $l = 1$ spherical Bessel function is calculated as

$$\begin{aligned}
 \int_0^\infty dz (j_1(z))^2 &= \int_0^\infty dz \frac{z^4 (j_1(z))^2}{z^4} \\
 &= -\frac{1}{3} z (j_1(z))^2 \Big|_0^\infty \\
 &\quad + \frac{1}{3} \int_0^\infty dz \frac{4z^3 (j_1(z))^2 + z^4 (2j_1(z)) (j_0(z) - \frac{2}{z}j_1(z))}{z^3} \\
 &= \frac{2}{3} \int_0^\infty dz z j_0(z) j_1(z) \\
 &= -\frac{2}{3} \int_0^\infty dz \sin(z) \frac{d}{dz} j_0(z) \\
 &= -\frac{2}{3} \sin(z) j_0(z) \Big|_0^\infty + \frac{2}{3} \int_0^\infty dz \frac{\sin(z) \cos(z)}{z}
 \end{aligned}$$

$$= \frac{\pi}{6} \quad , \quad (7.4.9)$$

where we have repeatedly used the regularity of the spherical Bessel functions at the origin and the $1/z$ behaviour at infinity. Finally, inserting the integral (7.4.9) into Eq. (7.4.8) we obtain the important result

$$\int d^3\mathbf{x}' \rho [g(\mathbf{x} - \mathbf{x}') - 1] = -1 \quad . \quad (7.4.10)$$

Hence, the exchange hole corresponds exactly to the charge of a single electron and for this reason the aforementioned combination of the electron and the exchange hole arising from the depletion of charge due to the Pauli principle has no charge.

7.5 Local correlation potential — parametrizations

So far we have derived and discussed the solution of the Jellium model as arising from first order perturbation theory. Still, we may well ask how these results change, if we include the electron-electron interaction to higher order. The corresponding correction to the ground state energy is named correlation energy, which is defined just as the difference between the exact and the first order or, equivalently, the Hartree-Fock result. As such the correlation energy actually has no physical significance but is rather a measure of the error due to the Hartree-Fock treatment.

Nevertheless, taking into account higher order perturbations is complicated by the fact that each higher order contribution diverges. Only in the limit of high densities ($r_s \rightarrow 0$) the complete perturbation series can be summed up, yielding the exact result first given by Gell-Mann and Brückner [58]

$$\frac{E}{N} = \frac{E^{(1)}}{N} + \frac{E_{corr}}{N} \quad , \quad (7.5.1)$$

with the correlation energy per particle given by

$$\begin{aligned} \frac{E_{corr}}{N} &= \left[\frac{2}{\pi} (1 - \ln 2) \ln r_s - 0.094 + \mathcal{O}(r_s \ln r_s) \right] \text{Ryd} \\ &= \left[0.0622 \ln r_s - 0.094 + \mathcal{O}(r_s \ln r_s) \right] \text{Ryd} \quad . \quad (7.5.2) \end{aligned}$$

The total ground energy per particle is shown in Fig. 7.10, where we have still included the zeroth and first order result growing out of the Sommerfeld model and the Hartree-Fock treatment of the Jellium model, respectively. Obviously, on inclusion of the correlation energy in the high density limit, the ground state energy stays to have a distinct minimum, which has shifted from the Hartree-Fock position of $r_s = 4.83a_B$ to the value $r_s = 3.83a_B$ with an energy of -0.099 Ryd rather than -0.095 Ryd. While the value for r_s is much closer to

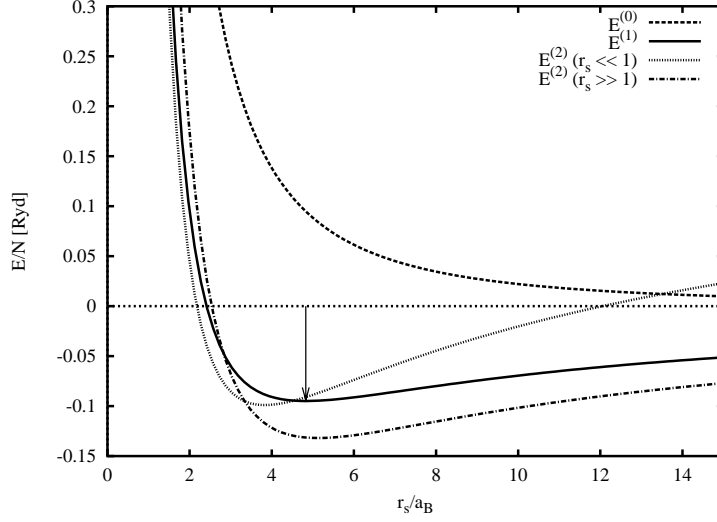


Figure 7.10: Ground state energy per particle of the Jellium model; while the curves labelled $E^{(2)}$ correspond to Eq. (7.5.2) and (7.5.3), respectively, the dotted and solid curves show the zeroth and first order result, respectively.

the experimental value for Na of $r_s = 3.96a_B$, the energy has hardly improved. Furthermore, we point to the strong increase of the ground state energy (7.5.2) for larger values of r_s , which, however, may be an artefact of the fact that the correlation energy (7.5.2) has been evaluated in the high density limit. That this is true becomes clear from the second curve labelled $E^{(2)}$ in Fig. 7.10, which grew out of a perturbation expansion in powers of $1/\sqrt{r_s}$ by Carr and coworkers, valid in the limit of small densities, hence, $r_s \gg 1$ [28, 29]. It resulted in an energy per particle given by

$$\begin{aligned} \frac{E}{N} = & -\frac{1.792}{r_s} + \frac{2.65}{r_s^{3/2}} - \frac{0.73}{r_s^2} + \left(\frac{21}{r_s} - \frac{4.8}{r_s^{3/4}} - \frac{1.16}{r_s^{5/4}} \right) e^{-2.06\sqrt{r_s}} \\ & - \left(\frac{2.06}{r_s^{5/4}} - \frac{0.66}{r_s^{7/4}} \right) e^{-1.55\sqrt{r_s}} . \end{aligned} \quad (7.5.3)$$

As is obvious from in Fig. 7.10 this leads to a considerable lowering of the energy per particle for low densities as compared to the result by Gell-Mann and Brückner and, hence, to a stabilization of the diluted homogeneous electron gas. Carr and coworkers complemented their result by an interpolation formula in order to make a connection between the high and low density results, which, however, we will not present here.

The calculation of the local correlation energy of the homogeneous electron gas has found much interest later on when it was used as part of the local density approximation usually employed in conjunction with density functional theory. This has motivated a great deal of work to find optimal parametrizations of

the correlation energy. We will postpone discussion of these approaches but will outline them in some detail in Sec. 10.1.

7.6 Local exchange potential — the X_α method

As already mentioned at the beginning of the present chapter the importance of the homogeneous electron gas stems from the fact that it allows for approximate treatments, which are exact in the limit of a constant ionic potential, hence, a constant electronic density, but still may remain in force for, at least slightly, inhomogeneous systems. Of course, simplifications are most desired for the exchange potential, which, according to Eq. (6.3.14) is a non-local potential. As a consequence, its calculation depends on the electronic wave function in all space, which fact hinders to consider larger systems.

For this reason it was a great step forward, when Slater proposed to replace the general non-local exchange potential (6.3.14) by a local one as growing out of the Jellium model [152]. Its derivation is rather straightforward, starting from the observation, that the single particle energies (7.3.26) can be interpreted as resulting from an exchange potential

$$v_{x,\sigma}(\mathbf{k}\sigma) = -\frac{k_{F\sigma}}{2\pi} \frac{e^2}{4\pi\epsilon_0} F\left(\frac{|\mathbf{k}|}{k_{F\sigma}}\right) . \quad (7.6.1)$$

The dependence of this potential on the particular plane wave state can be integrated out by averaging over all occupied states, i.e. over the Fermi sphere. We thus arrive at

$$\begin{aligned} v_{x,\sigma} &= -\frac{k_{F\sigma}}{2\pi} \frac{e^2}{4\pi\epsilon_0} \frac{3}{4\pi k_{F\sigma}^3} \int_{\Omega_{F\sigma}} d^3\mathbf{k} F\left(\frac{|\mathbf{k}|}{k_{F\sigma}}\right) \\ &= -\frac{3}{2\pi} \frac{e^2}{4\pi\epsilon_0} k_{F\sigma} \\ &= -\frac{3}{2\pi} \frac{e^2}{4\pi\epsilon_0} (6\pi^2 \rho_\sigma)^{\frac{1}{3}} , \end{aligned} \quad (7.6.2)$$

where we have used the identities (7.3.38) and (7.3.14). Finally, we reintroduce the dependence on the position and note for the local exchange potential the result

$$\begin{aligned} v_{x,\sigma}(\mathbf{r}) &= -\frac{3}{2\pi} \frac{e^2}{4\pi\epsilon_0} (6\pi^2 \rho_\sigma(\mathbf{r}))^{\frac{1}{3}} \\ &= -\frac{3}{2\pi} \frac{e^2}{4\pi\epsilon_0} (3\pi^2 \rho(\mathbf{r}))^{\frac{1}{3}} (1 + z_\sigma \xi)^{\frac{1}{3}} \\ &= -2.954 (a_B^3 \rho(\mathbf{r}))^{\frac{1}{3}} (1 + z_\sigma \xi)^{\frac{1}{3}} \text{Ryd} . \end{aligned} \quad (7.6.3)$$

Obviously, this local exchange potential favours regions of high electronic density and, hence, reflects the density dependence of the correct non-local potential (6.3.14).

Still, there has been some controversy over whether it is better to do the averaging in Eq. (7.6.2) over the whole Fermi sphere or over the Fermi surface only [152, 56, 91]. In the latter case, put forward by Kohn and Sham, the expression (7.6.2) has to be replaced by

$$\begin{aligned} V'_x &= -\frac{k_{F\sigma}}{2\pi} \frac{e^2}{4\pi\epsilon_0} \frac{1}{4\pi k_{F\sigma}^2} \int_{\Omega_{F\sigma}} d^3\mathbf{k} \delta(|\mathbf{k}| - k_{F\sigma}) F\left(\frac{|\mathbf{k}|}{k_{F\sigma}}\right) \\ &= -\frac{1}{\pi} \frac{e^2}{4\pi\epsilon_0} k_{F\sigma} \\ &= -\frac{1}{\pi} \frac{e^2}{4\pi\epsilon_0} (6\pi^2 \rho_\sigma)^{\frac{1}{3}}, \end{aligned} \quad (7.6.4)$$

which deviates from Eq. (7.6.2) by a factor of $\frac{2}{3}$. Nevertheless, realizing the approximate nature of the procedure, Slater suggested to introduce an adjustable parameter α (not to be mixed up with the parameter α used for the screened Coulomb potential in the preceding sections), which has to be fixed from observable quantities. Within the resulting, so-called X_α method the local exchange potential is then specified as

$$v_{x,\sigma}(\rho_\sigma(\mathbf{r})) = -\frac{3}{2\pi} \alpha \frac{e^2}{4\pi\epsilon_0} (6\pi^2 \rho_\sigma(\mathbf{r}))^{\frac{1}{3}}. \quad (7.6.5)$$

As has been demonstrated by a large number of calculations the dependence of the results on the parameter α is rather weak for values near $\frac{2}{3}$. Nevertheless, fixing its value from experimental data had the effect that this parameter was used to mimic electronic correlations in addition to mediating the correct exchange potential. A systematic study in this direction has been performed by Schwarz, who evaluated optimal α values for a large number of elemental systems [142].

Chapter 8

Thomas-Fermi theory

8.1 Electron density approach

A route completely different from Hartree-Fock theory was taken by Thomas and Fermi [163, 50, 51, 52], who abandoned direct use of the many-body wave function from their considerations but established the electron density as the central variable. Apart from the Sommerfeld model discussed in Sec. 3.1, Thomas-Fermi theory may thus be regarded as the first density functional theory, a fact, which justifies a deeper discussion. This is true despite the severe defects of Thomas-Fermi theory as e.g. the missing shell structure of atoms or the non-binding property pointed out in a landmark paper by Teller [161]. Eventually, these erroneous results motivated further research to go beyond Thomas-Fermi theory and thus paved the way for the development of density functional theory as it is known today.

In the present chapter we will outline the essentials of Thomas-Fermi theory, which will be necessary for the understanding of density functional theory. In doing so we will in the present section start with the basic formalism while postponing extensions to the following sections. We follow the representations by Parr and Yang, Jones and Gunnarsson as well as Eschrig [124, 84, 42]. A more formal description of Thomas-Fermi and related theories was given by Lieb [103]. Finally, the reader is referred to the elder review articles by Gombás and by March [61, 109, 110].

The basic idea underlying Thomas-Fermi theory is easily stated: Let us start out from the energy functional (6.1.24), which contains the kinetic energy, the external potential arising from the ions as well as the direct and exchange contributions to the electron-electron interaction,

$$\begin{aligned} \langle H_0 \rangle &= \sum_{\alpha} \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\ &\quad + \sum_{\sigma} \int d^3\mathbf{r} v_{ext}(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) \end{aligned}$$

$$+\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \left[\frac{\rho_\sigma(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{|\rho_{\sigma\sigma'}(\mathbf{r};\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \right] . \quad (8.1.1)$$

In using this Hartree-Fock expression we have accepted to exclude electron correlations from our considerations. In addition we will, for the time being, ignore the exchange term in order to keep the introduction of Thomas-Fermi theory as simple as possible. We will come back to the exchange term in Sec. 8.2.

Were it not for the kinetic energy term, the energy functional comprising, in addition, the external potential term and the classical Hartree contribution, could be expressed in terms of the electron density without need for the single particle wave functions. The crucial step towards further simplification was inspired by the success of the Sommerfeld theory discussed in Sec. 3.1, where we gave the kinetic energy of the homogeneous electron gas likewise in terms of the electron density. In particular, we derived the result (3.1.19) for the kinetic energy density. Using the notions outlined in Sec. 7.3, especially Eqs. (7.3.7) to (7.3.14), we easily extend the expression of the Sommerfeld model to spin-polarized systems and obtain

$$t_\sigma[\rho_\sigma] = C_{F\sigma} (\rho_\sigma)^{\frac{5}{3}} \quad , \quad (8.1.2)$$

where

$$C_{F\sigma} = \frac{3}{5} \frac{\hbar^2}{2m} (6\pi^2)^{\frac{2}{3}} \quad . \quad (8.1.3)$$

Generalizing this to arbitrary inhomogeneous electron densities we get for the kinetic energy functional

$$T[\rho] = \sum_\sigma C_{F\sigma} \int d^3\mathbf{r} (\rho_\sigma(\mathbf{r}))^{\frac{5}{3}} \quad , \quad (8.1.4)$$

which, when inserted into Eq. (8.1.1), gives rise to the Thomas-Fermi energy functional

$$\begin{aligned} \langle H_0 \rangle^{TF} &= \sum_\sigma C_{F\sigma} \int d^3\mathbf{r} (\rho_\sigma(\mathbf{r}))^{\frac{5}{3}} + \sum_\sigma \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho_\sigma(\mathbf{r}) \\ &+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_\sigma(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad . \end{aligned} \quad (8.1.5)$$

In contrast to the Hartree and Hartree-Fock functionals it is written solely in terms of the spin-dependent electronic densities. However, these densities themselves have not yet been determined. In the same manner as in the derivation of the Hartree or Hartree-Fock equations this is accomplished by combining the result (8.1.5) with the variational principle. Again, variation of the total energy functional is not completely free but subject to the condition of charge conservation,

$$\sum_\sigma \int d^3\mathbf{r} \rho_\sigma(\mathbf{r}) = N \quad , \quad (8.1.6)$$

where N is the total electron number. The variational equation thus assumes the form

$$\delta \left(\langle H_0 \rangle^{TF} - \sum_{\sigma} \mu_{\sigma} \int d^3 \mathbf{r} \rho_{\sigma}(\mathbf{r}) \right) \stackrel{!}{=} 0 \quad , \quad (8.1.7)$$

where μ_{σ} are Lagrange multipliers guaranteeing that Eq. (8.1.6) is fulfilled. Inserting Eq. (8.1.5) into Eq. (8.1.7) we arrive at

$$\begin{aligned} 0 \stackrel{!}{=} & \sum_{\sigma} C_{F\sigma} \int d^3 \mathbf{r} \delta (\rho_{\sigma}(\mathbf{r}))^{\frac{5}{3}} + \sum_{\sigma} \int d^3 \mathbf{r} v_{ext}(\mathbf{r}) \delta \rho_{\sigma}(\mathbf{r}) \\ & + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \delta \frac{\rho_{\sigma}(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \sum_{\sigma} \mu_{\sigma} \int d^3 \mathbf{r} \delta \rho_{\sigma}(\mathbf{r}) \quad . \end{aligned} \quad (8.1.8)$$

This variational equation must hold for any spatial dependence of the spin-dependent densities. As a consequence, we obtain the Thomas-Fermi equations

$$\frac{5}{3} C_{F\sigma} (\rho_{\sigma}(\mathbf{r}))^{\frac{2}{3}} + v_{ext}(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int d^3 \mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \mu_{\sigma} = 0 \quad . \quad (8.1.9)$$

Finally, using the definition of the Hartree potential,

$$v_H(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0} \int d^3 \mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad , \quad (8.1.10)$$

we cast the Thomas-Fermi equations into the form

$$\frac{5}{3} C_{F\sigma} (\rho_{\sigma}(\mathbf{r}))^{\frac{2}{3}} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) - \mu_{\sigma} = 0 \quad . \quad (8.1.11)$$

As they stand the Thomas-Fermi equations (8.1.9)/(8.1.11) provide a set of coupled integral equations (one for each spin), since the Hartree potential (8.1.10) still comprises the electron density in all space. For this reason, its solution must, in general, be achieved by iteration just in the same manner as in the Hartree and Hartree-Fock methods. However, we may still simplify the Thomas-Fermi approach, if we are dealing with a spin-degenerate system, in which case both spin-dependent densities reduce to half the electron density and we are able to replace Eq. (8.1.11) by

$$\frac{5}{3} C_F (\rho(\mathbf{r}))^{\frac{2}{3}} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) - \mu = 0 \quad , \quad (8.1.12)$$

where

$$C_F = \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2)^{\frac{2}{3}} \quad (8.1.13)$$

and

$$\mu = \mu_{\uparrow} = \mu_{\downarrow} \quad . \quad (8.1.14)$$

The spin-degenerate form (8.1.12) of the Thomas-Fermi equation may be substantially simplified by employing, in addition, Poisson's equation,

$$-\nabla^2 v_H(\mathbf{r}) = \frac{e^2}{\epsilon_0} \rho(\mathbf{r}) \quad . \quad (8.1.15)$$

Combining this with Eq. (8.1.12) and using Eq. (8.1.13) we arrive at the final result

$$-\nabla^2 v_H(\mathbf{r}) = \frac{e^2}{3\pi^2\epsilon_0} \left([\mu - v_{ext}(\mathbf{r}) - v_H(\mathbf{r})] \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \quad , \quad (8.1.16)$$

which is a differential equation for the Hartree potential.

Compared to the Hartree or Hartree-Fock equations the Thomas-Fermi equations (8.1.11) or, in case of spin-degeneracy, Eqs. (8.1.13) and (8.1.16), represent indeed a considerable simplification: Instead of having to solve an eigenvalue problem with $3N$ coordinates we are left with only two integral equations for the three-dimensional electron densities. However, the price for this advantage is high. As a matter of fact, Thomas-Fermi theory fails to predict the shell structure of atoms and, hence, cannot describe the similar properties of atoms falling into the same row of the periodic table. Moreover, it is unable to account for the binding of atoms into molecules or solids [161], and it produces an infinite charge density at the nucleus. To overcome these serious deficiencies was the aim of several improvements of Thomas-Fermi theory, which proceeded mainly into two different directions.

8.2 Thomas-Fermi-Dirac theory

In their original work, Thomas and Fermi modelled the electron-electron interaction by only the classical electrostatic contribution and excluded both the exchange term as well as electronic correlations. We have followed this line in the previous section in order to keep the presentation of Thomas-Fermi theory as simple as possible. However, the aforementioned shortcomings of the theory called for extensions. In the present section we will concentrate on the exchange contribution, which was included into Thomas-Fermi theory by Dirac [36], this resulting in what is now called Thomas-Fermi-Dirac theory.

To be specific, we start out from the exchange contribution to the total energy functional, which we already included as the last term in Eq. (8.1.1) and which reads as

$$\langle H_0 \rangle^{(x)} = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{|\rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad . \quad (8.2.1)$$

Here we have used the representation in terms of the spin-dependent density matrix. Of course, the spirit of Thomas-Fermi theory requires rather a representation in terms of the electron density. A solution to this problem was proposed by Dirac, who approximated the spin-dependent density matrix by

the expression (7.4.4) arising from the homogeneous electron gas and only at the very end reintroduced the spatial dependence of the electron density. Inserting the identity (7.4.4) into Eq. (8.2.1) and repeatedly using Eq. (7.3.8) we obtain

$$\begin{aligned}
\langle H_0 \rangle^{(x)} &= -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \delta_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{k_{F\sigma}^6 (j_1(k_F|\mathbf{r}-\mathbf{r}'|))^2}{4\pi^4 k_{F\sigma}^2 (|\mathbf{r}-\mathbf{r}'|)^3} \\
&= -\frac{9}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \delta_{\sigma\sigma'} \int d^3\mathbf{r} (\rho_\sigma(\mathbf{r}))^2 \frac{1}{k_{F\sigma}^2} \int d^3\mathbf{z} \frac{(j_1(|\mathbf{z}|))^2}{|\mathbf{z}|} \\
&= -\frac{9}{2} \frac{4\pi}{(6\pi^2)^{\frac{2}{3}}} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \delta_{\sigma\sigma'} \int d^3\mathbf{r} (\rho_\sigma(\mathbf{r}))^{\frac{4}{3}} \int_0^\infty dz \frac{(j_1(z))^2}{z} ,
\end{aligned} \tag{8.2.2}$$

where we have used $\mathbf{z} = k_{F\sigma}(\mathbf{r} - \mathbf{r}')$. In order to solve the integral containing the spherical Bessel function we fall back on a wealth of identities for these functions, in particular, [1, Eq. 10.1.22]

$$f_{l+1}(z) = \left(-\frac{\partial}{\partial z} + \frac{l}{z} \right) f_l(z) \tag{8.2.3}$$

as well as [1, Eq. 10.1.21]

$$f_{l-1}(z) = \left(\frac{\partial}{\partial z} + \frac{l+1}{z} \right) f_l(z) , \tag{8.2.4}$$

which are valid for any linear combination of a spherical Bessel function j_l and a spherical Neumann function n_l . From these identities we obtain

$$\frac{\partial j_0(z)}{\partial z} = -j_1(z) \tag{8.2.5}$$

and

$$\frac{\partial^2 j_0(z)}{\partial z^2} = -\frac{\partial j_1(z)}{\partial z} = \frac{2}{z} j_1(z) - j_0(z) = -\frac{2}{z} \frac{\partial j_0(z)}{\partial z} - j_0(z) . \tag{8.2.6}$$

Inserting these formulas into the integral entering Eq. (8.2.2) we arrive at

$$\begin{aligned}
\int_0^\infty dz \frac{(j_1(z))^2}{z} &= \int_0^\infty dz \frac{\partial j_0(z)}{\partial z} \frac{1}{z} \frac{\partial j_0(z)}{\partial z} \\
&= \int_0^\infty dz \frac{\partial j_0(z)}{\partial z} \left(-\frac{1}{2} j_0(z) - \frac{1}{2} \frac{\partial^2 j_0(z)}{\partial z^2} \right) \\
&= -\frac{1}{4} \int_0^\infty dz \frac{\partial}{\partial z} \left[(j_0(z))^2 + \left(\frac{\partial j_0(z)}{\partial z} \right)^2 \right] \\
&= -\frac{1}{4} \left[(j_0(z))^2 + \left(\frac{\partial j_0(z)}{\partial z} \right)^2 \right]_0^\infty \\
&= \frac{1}{4} .
\end{aligned} \tag{8.2.7}$$

Here we have employed the $\frac{1}{z}$ behaviour of the spherical Bessel functions for large arguments as well as the fact that the functions vanish at the origin for $l \geq 1$. In contrast, j_0 approaches unity for $z \rightarrow 0$.

Finally, inserting the integral (8.2.7) into the exchange energy functional (8.2.2), we arrive at the result

$$\langle H_0 \rangle^{(x)} = -\frac{9\pi}{2} \frac{1}{(6\pi^2)^{\frac{2}{3}}} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma} \int d^3\mathbf{r} (\rho_{\sigma}(\mathbf{r}))^{\frac{4}{3}} \quad . \quad (8.2.8)$$

For spin-degenerate systems it reduces to

$$\langle H_0 \rangle^{(x)} = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r} (\rho(\mathbf{r}))^{\frac{4}{3}} \quad , \quad (8.2.9)$$

which is identical to the formula given by Dirac [36].

Combining the result (8.2.8) with the total energy functional (8.1.5) we obtain the Thomas-Fermi-Dirac energy functional

$$\begin{aligned} \langle H_0 \rangle^{TFD} &= \sum_{\sigma} C_{F\sigma} \int d^3\mathbf{r} (\rho_{\sigma}(\mathbf{r}))^{\frac{5}{3}} + \sum_{\sigma} \int d^3\mathbf{r} v_{ext}(\mathbf{r}) \rho_{\sigma}(\mathbf{r}) \\ &+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &- \frac{e^2}{4\pi\epsilon_0} C_{x\sigma} \sum_{\sigma} \int d^3\mathbf{r} (\rho_{\sigma}(\mathbf{r}))^{\frac{4}{3}} \quad , \end{aligned} \quad (8.2.10)$$

where we have abbreviated

$$C_{x\sigma} = -\frac{9\pi}{2} \frac{1}{(6\pi^2)^{\frac{2}{3}}} \quad . \quad (8.2.11)$$

As in Thomas-Fermi theory this functional, when combined with the charge conservation condition (8.1.7) and used with a variational principle, gives rise to Euler-Lagrange equations, the Thomas-Fermi-Dirac equations

$$\frac{5}{3} C_{F\sigma} (\rho_{\sigma}(\mathbf{r}))^{\frac{2}{3}} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0} C_{x\sigma} \frac{4}{3} (\rho_{\sigma}(\mathbf{r}))^{\frac{1}{3}} - \mu_{\sigma} = 0 \quad . \quad (8.2.12)$$

Here, we have already used the definition (8.1.10) of the Hartree potential. In contrast to the situation in Thomas-Fermi theory the exchange contribution hinders a simple solution of this equation for spin-degenerate systems as that sketched at the end of the previous section. For this reason, Eq. (8.2.12) must be solved self-consistently. We will not go into the details in the present context but rather summarize the many calculations using the Thomas-Fermi-Dirac functional to the fact that inclusion of the exchange term did not lead to a substantial improvement of the theory.

8.3 Gradient correction

The rather limited success of Thomas-Fermi-Dirac theory lead von Weizsäcker to propose a yet different improvement. Instead of including additional potential contributions, von Weizsäcker aimed at the homogeneous electron gas expression of the kinetic energy. In order to improve on this term he included a new term, which contained the gradient of the density, this resulting in the so-called Thomas-Fermi-Dirac-Weizsacker functional

$$\begin{aligned}
 \langle H_0 \rangle^{TFDW} &= \sum_{\sigma} C_{F\sigma} \int d^3\mathbf{r} (\rho_{\sigma}(\mathbf{r}))^{\frac{5}{3}} + \lambda \frac{\hbar^2}{16m} \sum_{\sigma} \int d^3\mathbf{r} \frac{|\nabla\rho_{\sigma}(\mathbf{r})|^2}{\rho_{\sigma}(\mathbf{r})} \\
 &+ \sum_{\sigma} \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho_{\sigma}(\mathbf{r}) \\
 &+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
 &- \frac{e^2}{4\pi\epsilon_0} C_{x\sigma} \sum_{\sigma} \int d^3\mathbf{r} (\rho_{\sigma}(\mathbf{r}))^{\frac{4}{3}} \quad . \quad (8.3.1)
 \end{aligned}$$

While von Weizsäcker used a value of 1 for the parameter λ , later work suggested that a smaller value of 1/9 or 1/5 might be a better choice. As before the functional (8.3.1) gives rise to Euler-Lagrange equations, the Thomas-Fermi-Dirac-Weizsacker equations

$$\begin{aligned}
 \frac{5}{3} C_{F\sigma} (\rho_{\sigma}(\mathbf{r}))^{\frac{2}{3}} + \lambda \frac{\hbar^2}{16m} \left[\frac{|\nabla\rho_{\sigma}(\mathbf{r})|^2}{(\rho_{\sigma}(\mathbf{r}))^2} - 2 \frac{\Delta\rho_{\sigma}(\mathbf{r})}{\rho_{\sigma}(\mathbf{r})} \right] \\
 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) - \frac{e^2}{4\pi\epsilon_0} C_{x\sigma} \frac{4}{3} (\rho_{\sigma}(\mathbf{r}))^{\frac{1}{3}} - \mu_{\sigma} = 0 \quad . \quad (8.3.2)
 \end{aligned}$$

Here, we have again used the definition (8.1.10) of the Hartree potential.

As it turned out in many subsequent investigations inclusion of the gradient term improved the situation a lot. Instead of diverging the electron density at the nucleus assumes a finite value and it decays exponentially far away from it. Furthermore, Teller's non-binding theorem is invalidated by the von Weizsäcker correction and stable molecular binding became possible. Yet, due to numerical difficulties, there still remain doubts about this latter issue.

Nevertheless, the substantial improvements of Thomas-Fermi theory on inclusion of the von Weizsäcker gradient correction point to the fact that the most severe errors coming with its original version arise from the treatment of the kinetic energy functional. Obviously, representing this functional in terms of the expression arising from the homogeneous electron gas brings us too far off from the truth once we are dealing with inhomogeneous systems. It was this finding, which, eventually inspired Hohenberg, Kohn, and Sham to aim, in particular, at a more careful handling of the kinetic energy.

8.4 Thomas-Fermi screening

In its original form presented in Sec. 8.1 Thomas-Fermi theory is particularly suited to discuss the effect of screening. To this end we start out from the homogeneous electron gas, where the ionic charge density is smeared out to give a positive background neutralizing the electronic charge density and where, by construction, Thomas-Fermi theory is exact. We note

$$\rho(\mathbf{r}) \stackrel{!}{=} \rho \quad . \quad (8.4.1)$$

In addition, the total potential seen by the electrons likewise is constant,

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) \stackrel{!}{=} v_{eff} \quad . \quad (8.4.2)$$

Note that the ionic and the Hartree potential themselves are not constant, since they must obey the respective Poisson equation and thus have a constant Laplacian derivative. Combining Eqs. (8.1.12) and (8.1.13) for the homogeneous gas and using Eq. (3.1.11) we write

$$\begin{aligned} \frac{e^2}{\epsilon_0} \rho &= -\nabla^2 v_H(\mathbf{r}) = \frac{e^2}{3\pi^2 \epsilon_0} \left([\mu - v_{eff}] \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \\ &= \frac{e^2}{3\pi^2 \epsilon_0} \left(E_F \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \quad . \end{aligned} \quad (8.4.3)$$

Next we place into this ensemble a small test charge δZ at $\mathbf{r} = \mathbf{0}$. It will generate an external potential

$$\delta v_{ext}(\mathbf{r}) = -\delta \frac{Z}{|\mathbf{r}|} \quad , \quad (8.4.4)$$

which adds to the ionic potential. For $\mathbf{r} \neq \mathbf{0}$ the Laplacian $\nabla^2 \delta v_{ext}(\mathbf{r})$ of this potential vanishes and we thus have

$$\nabla^2 \delta v_H(\mathbf{r}) = \nabla^2 \delta v_{eff}(\mathbf{r}) \quad \text{for } \mathbf{r} \neq \mathbf{0} \quad . \quad (8.4.5)$$

Inserting these identities into the formulation (8.1.13) of the Thomas-Fermi equation we arrive at

$$\begin{aligned} -\nabla^2 (v_H(\mathbf{r}) + \delta v_H(\mathbf{r})) &= -\nabla^2 (v_H(\mathbf{r}) + \delta v_{eff}(\mathbf{r})) \\ &= \frac{e^2}{3\pi^2 \epsilon_0} \left([\mu - v_{eff} - \delta v_{eff}(\mathbf{r})] \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \\ &= \frac{e^2}{3\pi^2 \epsilon_0} \left([E_F - \delta v_{eff}(\mathbf{r})] \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \\ &\approx \frac{e^2}{3\pi^2 \epsilon_0} \left(E_F \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \left(1 - \frac{3}{2} \frac{\delta v_{eff}(\mathbf{r})}{E_F} \right) \quad , \end{aligned} \quad (8.4.6)$$

where the last step grew out of the first order Taylor expansion. Comparison to the corresponding equation (8.4.3) for the homogeneous system yields an equation for the additional potential

$$\begin{aligned}\nabla^2 \delta v_{eff}(\mathbf{r}) &= \frac{e^2}{2\pi^2 \epsilon_0} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E_F} \delta v_{eff}(\mathbf{r}) \\ &=: k_{TF}^2 \delta v_{eff}(\mathbf{r}) \quad .\end{aligned}\tag{8.4.7}$$

Here we have in the last step defined the Thomas-Fermi screening wave vector. We point out that the disturbance due to the test charge at $\mathbf{r} = \mathbf{0}$ leads to a spherical symmetric additional potential $\delta v_{eff}(|\mathbf{r}|)$. As well known, the solutions of Eq. (8.4.7) are spherical Hankel functions times spherical harmonics for angular momentum $l = 0$ and the radial part of the spherical symmetric potential is thus given by

$$\delta v_{eff}(\mathbf{r}) = \frac{e^{-k_{TF} r}}{r} \quad ,\tag{8.4.8}$$

which is a Yukawa-type potential. Note that strictly speaking this result holds only for large distances r from the test charge, where the potential $\delta v_{eff}(\mathbf{r})$ and the above Taylor expansion justified.

With the help of Eq. (3.1.11) the Thomas-Fermi screening wave vector may be written as

$$k_{TF}^2 = \frac{e^2}{2\pi^2 \epsilon_0} \frac{2m}{\hbar^2} k_F \quad ,\tag{8.4.9}$$

which leads to

$$\frac{k_{TF}^2}{k_F^2} = \frac{e^2}{4\pi^2 \epsilon_0} \frac{m}{\hbar^2} \frac{4}{\pi} \frac{1}{k_F} = \frac{4}{\pi} \left(\frac{4}{9\pi} \right)^{\frac{1}{3}} \frac{r_s}{a_B} \quad .\tag{8.4.10}$$

It is instructive to define the Thomas-Fermi screening length

$$\lambda_{TF}^2 = \frac{1}{k_{TF}^2} = \frac{2\pi^2 \epsilon_0}{e^2} \frac{\hbar^2}{2m} \frac{1}{k_F} \quad .\tag{8.4.11}$$

Using Eqs. (3.1.9) and (3.1.10) we get

$$\frac{\lambda_{TF}}{a_B} = \left(\frac{\pi}{12} \right)^{\frac{1}{3}} \sqrt{\frac{r_s}{a_B}} \quad .\tag{8.4.12}$$

In ordinary metals, r_s/a_B varies between 2 and 6 and the Thomas-Fermi screening length turns out to be similar to the Bohr radius. Thus the screening of the test charge by the surrounding electronic density is highly effective.

Chapter 9

Density functional theory

9.1 The Hohenberg-Kohn theorems

Since its introduction in 1964-1965 by Hohenberg, Kohn, and Sham density functional theory (DFT) [80, 91] has become one of the major tools for understanding materials properties. As such, it has had a decisive impact not only on the field of electronic structure calculations in particular but has strongly influenced condensed matter physics in general. This is, of course, due to the incredible success in accurately predicting especially ground state properties of numerous systems. Nevertheless, to a similar extent it traces back to the conceptual simplicity underlying DFT, which allows for a very efficient use of computational resources even for large systems comprising of the order of 1000 electrons. Although most applications have been for solids the theory has been likewise successfully used for atoms and molecules, where it competes with standard quantum chemical methods.

As the name suggests, the electronic density is the central variable of DFT, which therefore avoids the problem of calculating the ground-state many-body wave function. The general approach of DFT is thus identical to its predecessor, Thomas-Fermi theory, which, however, failed in correctly describing the kinetic energy and in properly including exchange and correlation. At the same time, in using the electronic density, DFT goes beyond Hartree-Fock theory, which takes only a single Slater determinant, hence, only one particular electronic configuration into consideration. While being an exact approach to the ground state density functional theory replaces computation of the many-body wave function by that of single-particle wave functions, a much easier task. In other words, DFT formally casts the full problem posed by the system of interaction electrons into an effective single-particle problem. Yet, we have to be aware that this step might hinder gaining deeper insight into the effect of electron-electron interactions and so far lead to an unsatisfactory description of strongly interacting electron systems.

While the original formulation by Hohenberg and Kohn was for non-degenerate electronic ground states, DFT has since then been extended to degenerate

ground states, spin-polarized and relativistic systems or to finite temperatures. At the same time, it has been tightly connected to a firm mathematical basis. In the present chapter we will outline the most important aspects of DFT. In doing so we start out with the basic formalism. Application of the theory leads directly to the local density approximation (LDA) but we will also include more recent approaches to the interacting electron system as e.g. the generalized gradient approximation (GGA) or the exact treatment of the exchange interaction (EXX) in the following chapter.

While an excellent overview over density functional theory and related approaches may be found in Fulde's book [55], more detailed accounts with special emphasis on DFT were given by Kohn and Vashishta [92], Williams and von Barth [171], von Barth [14, 15, 16], Jones and Gunnarsson [84], Dreizler and Gross [38, 37, 64], Kryachko and Ludeña [97], Parr and Yang [124], Eschrig [42], as well as March [111], just to mention a few. Finally, a compilation of review articles on density functional theory is given in Appendix G of the book by Parr and Yang [124].

Before going into the details we prepare the field and restate the basic identities needed throughout in this chapter. To be specific, we start out again from the Hamiltonian (7.1.1) as arising from the Born-Oppenheimer approximation, which we now write as

$$\begin{aligned} H_0 &= H_{ion-ion}(\{\mathbf{R}_\mu\}) + H_{el}(\{\mathbf{r}_i\}) + H_{ion-el}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= H_{el,kin}(\{\mathbf{r}_i\}) + H_{ext}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) + H_{el-el}(\{\mathbf{r}_i\}) \quad , \quad (9.1.1) \end{aligned}$$

where

$$H_{el,kin}(\{\mathbf{r}_i\}) = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 \right] \quad , \quad (9.1.2)$$

$$H_{el-el}(\{\mathbf{r}_i\}) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad , \quad (9.1.3)$$

$$\begin{aligned} H_{ext}(\{\mathbf{r}_i\}) &= H_{ion-ion}(\{\mathbf{R}_\mu\}) + H_{ion-el}(\{\mathbf{r}_i, \mathbf{R}_\mu\}) \\ &= \frac{1}{2} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} V_{ion-ion}(\mathbf{R}_\mu - \mathbf{R}_\nu) + \sum_i \left[\sum_\mu V_{ion-el}(\mathbf{r}_i - \mathbf{R}_\mu) \right] \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z_{val,\mu} Z_{val,\nu}}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} - \frac{e^2}{4\pi\epsilon_0} \sum_\mu \sum_i \frac{Z_{val,\mu}}{|\mathbf{R}_\mu - \mathbf{r}_i|} \\ &=: \sum_i v_{ext}(\mathbf{r}_i) \quad . \quad (9.1.4) \end{aligned}$$

\mathbf{R}_μ and \mathbf{r}_i denote, as usual, the positions of the ions and electrons, respectively. In the last step we have specified the Coulombic nature of the ion-ion interaction, $Z_{val,\mu}$ being the number of valence electrons provided by the μ 'th ion. Since this latter interaction, as discussed in Sec. 7.1, adds only a constant

to the potential seen by the electrons we have absorbed it into the ion-electron interaction, which acts like an external potential. As already mentioned in Sec. 4.1 the term “external” refers to the fact that this potential is generated by (ionic) charges, which are independent of the electronic charge density. Note that, in the same manner as in Sec. 7.1 for the homogeneous electron gas, we have correctly included the ion-ion interaction in the Hamiltonian, where it counterbalances the long-range Coulombic electron-electron interaction. We point, however, to our discussion in Sec. 7.1 on the correct cancellation of these terms, which qualitatively applies also to the inhomogeneous electron gas.

In the form (9.1.1) to (9.1.4) the Hamiltonian consists of three main contributions, namely the kinetic energy of the electrons, their mutual Coulomb interaction and an external potential acting onto the electrons. The actual shape of the latter will not be crucial for all that follows. Finally, we still identify one- and two-particle contributions to the Hamiltonian,

$$H_0^{\{1\}} = H_{el,kin}(\{\mathbf{r}_i\}) + H_{ext}(\{\mathbf{r}_i\}) \quad , \quad (9.1.5)$$

$$H_0^{\{2\}} = H_{el-el}(\{\mathbf{r}_i\}) \quad (9.1.6)$$

as in Eq. (4.1.6).

In addition to the Hamiltonian we need the electron density operator as growing out of the definitions (5.7.6) and (5.7.11) as

$$\begin{aligned} \hat{\rho}(\mathbf{r}) &= \sum_{\sigma} \hat{\rho}_{\sigma}(\mathbf{r}) \\ &= \sum_{\sigma} \psi_{\sigma}^{\dagger}(\mathbf{r}) \psi_{\sigma}(\mathbf{r}) \\ &= \sum_{\sigma} \sum_{\alpha\beta} \chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\beta;\sigma}(\mathbf{r}) a_{\alpha}^{\dagger} a_{\beta} \\ &= \sum_{\sigma} \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \delta_{\sigma\sigma_i} \quad , \end{aligned} \quad (9.1.7)$$

from which the ground state electron density is calculated according to Eq. (5.7.14) as

$$\begin{aligned} \rho_0(\mathbf{r}) = \sum_{\sigma} \rho_{0,\sigma}(\mathbf{r}) &= \sum_{\sigma} \langle \Psi_0 | \hat{\rho}_{\sigma}(\mathbf{r}) | \Psi_0 \rangle \\ &= \sum_{\sigma} \sum_{\alpha} |\chi_{\alpha;\sigma}(\mathbf{r})|^2 n_{\alpha} \quad , \end{aligned} \quad (9.1.8)$$

where $|\Psi_0\rangle$ and n_{α} denote the ground-state wave function and the occupation number of the single-particle state χ_{α} . Only for non-interacting particles, when the many-body state reduces to a single Slater determinant, the occupation numbers n_{α} are one and zero, respectively and Eq. (9.1.8) reduces to

$$\rho_0(\mathbf{r}) = \sum_{\sigma} \sum_{\alpha}^{occ} |\chi_{\alpha;\sigma}(\mathbf{r})|^2 \quad . \quad (9.1.9)$$

Finally, the electronic density should be normalized according to the condition

$$N[\rho] = \int d^3\mathbf{r} \rho(\mathbf{r}) = N \quad . \quad (9.1.10)$$

Following Eq. (5.6.26) we complement Eqs. (9.1.2) to (9.1.4) by the corresponding expressions in terms of electron field operators as defined by Eqs. (5.7.4) and (5.7.5),

$$\begin{aligned} H_{el,kin} &= \sum_{\sigma} \int d^3\mathbf{r} \psi_{\sigma}^{\dagger}(\mathbf{r}) \left\{ -\frac{\hbar^2}{2m} \nabla^2 \right\} \psi_{\sigma}(\mathbf{r}) \\ &= \sum_{\sigma} \int d^3\mathbf{r} \left\{ \frac{\hbar^2}{2m} [\nabla \psi_{\sigma}^{\dagger}(\mathbf{r})] \cdot [\nabla \psi_{\sigma}(\mathbf{r})] \right\} \quad , \end{aligned} \quad (9.1.11)$$

$$\begin{aligned} H_{el-el} &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \psi_{\sigma}^{\dagger}(\mathbf{r}) \psi_{\sigma'}^{\dagger}(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_{\sigma'}(\mathbf{r}') \psi_{\sigma}(\mathbf{r}) \quad , \\ & \quad (9.1.12) \end{aligned}$$

$$\begin{aligned} H_{ext} &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z_{val,\mu} Z_{val,\nu}}{|\mathbf{R}_{\mu} - \mathbf{R}_{\nu}|} \\ &\quad + \sum_{\sigma} \int d^3\mathbf{r} \psi_{\sigma}^{\dagger}(\mathbf{r}) \left\{ \sum_{\mu} V_{ion-el}(\mathbf{r} - \mathbf{R}_{\mu}) \right\} \psi_{\sigma}(\mathbf{r}) \\ &= \frac{1}{2N} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z_{val,\mu} Z_{val,\nu}}{|\mathbf{R}_{\mu} - \mathbf{R}_{\nu}|} \int d^3\mathbf{r} \hat{\rho}(\mathbf{r}) \\ &\quad - \frac{e^2}{4\pi\epsilon_0} \sum_{\mu} \int d^3\mathbf{r} \frac{Z_{val,\mu}}{|\mathbf{R}_{\mu} - \mathbf{r}|} \hat{\rho}(\mathbf{r}) \\ &=: \int d^3\mathbf{r} v_{ext}(\mathbf{r}) \hat{\rho}(\mathbf{r}) \quad . \end{aligned} \quad (9.1.13)$$

After these preparations we are in a position to turn to the basic ideas of density functional theory as presented by Hohenberg and Kohn, who concentrated on a local, spin-independent potential and assumed the ground state to be non-degenerate. While establishing the electronic ground state density as the central variable they then formulated the following two theorems:

1. The external potential $v_{ext}(\mathbf{r})$ is determined, apart from a trivial constant, by the electronic ground state density $\rho_0(\mathbf{r})$.
2. The total energy functional $E[\rho]$ has a minimum equal to the ground state energy at the ground state density.

While the first theorem stresses the more fundamental aspects the second one is of great practical importance as it allows to formulate a variational principle in terms of the density and thus will open the way to single-particle equations.

Before we prove the aforementioned theorems we point out that the kinetic energy (9.1.2) of the electrons as well as their mutual interaction (9.1.3) are universal in as far as these operators are the same for all systems of interacting electrons. For the same reason the functional

$$F[\rho] = \langle \Psi | H_{el,kin}(\{\mathbf{r}_i\}) + H_{el-el}(\{\mathbf{r}_i\}) | \Psi \rangle \quad , \quad (9.1.14)$$

which does not explicitly depend on the external potential, is a universal functional of the electronic density. The only non-universal contribution to the Hamiltonian stems from the external potential (9.1.4), which, hence, alone invokes changes of the electronic wave function on going from one electronic system to another. In other words, once the external potential has been specified the Hamiltonian is completely determined. Actually, this result is not surprising since the external potential arises from the Coulomb potential of the nuclei, to which the electrons respond by balancing their kinetic and mutual interaction energy both contained in the functional $F[\rho]$. In passing, we complement Eq. (9.1.14) by the following expression for the functional due to the external potential,

$$\langle \Psi | H_{ext}(\{\mathbf{r}_i\}) | \Psi \rangle = \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \quad , \quad (9.1.15)$$

which follows directly from combining Eqs. (9.1.8) and (9.1.13) and will be used below.

Next we recall that the ground state $|\Psi_0\rangle$ arises from the variational principle by minimizing the total energy $\langle \Psi_0 | H_0 | \Psi_0 \rangle$ (note the normalization (9.1.10) above). Assuming for the time being that the electronic ground state is non-degenerate, we are thus able to uniquely determine the ground state wave function and, according to Eq. (9.1.8), the electronic ground state density from knowledge of the external potential and, of course, of the total electron number N . We cast this fact into the relation

$$v_{ext}(\mathbf{r}) \xrightarrow{(1)} |\Psi_0\rangle \xrightarrow{(2)} \rho_0(\mathbf{r}) \quad . \quad (9.1.16)$$

Thus the variational principle as well as Eq. (9.1.8) establish surjective maps from the set of local single-particle potentials $v_{ext}(\mathbf{r})$ to the set of ground state wave functions $|\Psi_0\rangle$ and from the latter set to the set of ground state densities $\rho_0(\mathbf{r})$, respectively.

The first theorem of Hohenberg and Kohn reverts the previous relationship and adds to Eq. (9.1.16) the injective map of the quantities involved. The original proof, again for non-degenerate ground states, proceeds by *reductio ad absurdum*. Assume two external potentials $v_{ext}(\mathbf{r})$ and $v'_{ext}(\mathbf{r})$ differing by more than a trivial constant to exist, which give rise to the same electronic ground state density $\rho_0(\mathbf{r})$. Since the external potentials define two different Hamiltonians H_0 and H'_0 , the calculated ground state wave functions $|\Psi_0\rangle$ and $|\Psi'_0\rangle$ as growing out of different Schrödinger equations must differ. We thus get from the variational principle for the ground state

$$E' = \langle \Psi'_0 | H'_0 | \Psi'_0 \rangle$$

$$\begin{aligned}
&< \langle \Psi_0 | (H'_0) | \Psi_0 \rangle \\
&= \langle \Psi_0 | H_0 + H'_{ext} - H_{ext} | \Psi_0 \rangle \quad , \quad (9.1.17)
\end{aligned}$$

hence,

$$E' < E + \int d^3\mathbf{r} [v'_{ext}(\mathbf{r}) - v_{ext}(\mathbf{r})] \rho(\mathbf{r}) \quad . \quad (9.1.18)$$

Interchanging primed and unprimed quantities we arrive at

$$E < E' + \int d^3\mathbf{r} [v_{ext}(\mathbf{r}) - v'_{ext}(\mathbf{r})] \rho'(\mathbf{r}) \quad , \quad (9.1.19)$$

and, on adding the previous two inequalities under the condition $\rho(\mathbf{r}) = \rho'(\mathbf{r})$ we obtain the inconsistency

$$E + E' < E + E' \quad . \quad (9.1.20)$$

To conclude, apart from a trivial constant the external potential $v_{ext}(\mathbf{r})$ is a unique functional of the electronic density $\rho(\mathbf{r})$. Since, as mentioned above, the external potential fixes the Hamiltonian (9.1.1) to (9.1.7) all ground state properties are unique functionals of the electronic density.

While performing the previous proof we have actually implied that the map from the external potential onto the ground state wave functions *is* injective. This assumption went into the arguments preceding Eq. (9.1.17). In contrast, Eqs. (9.1.17) to (9.1.20) relate the electronic density to the ground state wave function rather than to the external potential, which cancels out on adding Eqs. (9.1.18) and (9.1.19) due to the required identity of the densities. In other words, from the above proof we have only that the map (2) of Eq. (9.1.16) is injective.

In order to show that injectivity holds true also for the map (1) of Eq. (9.1.16) we again proceed by *reductio ad absurdum* and assume two external potentials $v_{ext}(\mathbf{r})$ and $v'_{ext}(\mathbf{r})$ to exist, which differ by more than a trivial constant. These give rise to the Schrödinger equations

$$\begin{aligned}
H_0 |\Psi_0\rangle &= [H_{el,kin} + H_{ext} + H_{el-el}] |\Psi_0\rangle \\
&= E |\Psi_0\rangle \quad , \quad (9.1.21)
\end{aligned}$$

$$\begin{aligned}
H'_0 |\Psi'_0\rangle &= [H_{el,kin} + H'_{ext} + H_{el-el}] |\Psi'_0\rangle \\
&= E' |\Psi'_0\rangle \quad . \quad (9.1.22)
\end{aligned}$$

Requiring that $|\Psi_0\rangle = |\Psi'_0\rangle$ and subtracting the previous identities we get

$$[H_{ext} - H'_{ext}] |\Psi_0\rangle = [E - E'] |\Psi_0\rangle \quad . \quad (9.1.23)$$

Since the external potentials are multiplicative operators we obtain

$$H_{ext} - H'_{ext} = E - E' \quad , \quad (9.1.24)$$

unless the ground state wave function vanishes in a region of finite measure. This, however, will not happen for well-behaved potentials without e.g. infinite

potential barriers. As a consequence of Eq. (9.1.24) the potentials differ only by a constant in contradiction to the above assumption. To sum up, also the map (1) of Eq. (9.1.16) is injective and, taking all previous results together, both maps are bijective,

$$v_{ext}(\mathbf{r}) \xleftrightarrow{(1)} |\Psi_0\rangle \xleftrightarrow{(2)} \rho_0(\mathbf{r}) \quad . \quad (9.1.25)$$

It was one of the main goals of Hohenberg and Kohn to make these relationships explicit. Finally, since, by virtue of Eq. (9.1.25), both the external potential and the ground state wave function are unique functionals of the electron density, we may cast the first theorem of Hohenberg and Kohn into a form, which stresses the decisive role of the electron density,

1. The ground state expectation value of any observable \hat{A} is a unique functional of the ground state density,

$$A_0[\rho] = \langle \Psi_0[\rho_0] | \hat{A} | \Psi_0[\rho_0] \rangle \quad . \quad (9.1.26)$$

This formulation applies, in particular, to the universal functional $F[\rho]$ as given by Eq. (9.1.14) and thus the total energy functional is completely determined. Of course, this is quite plausible, since the density fixes the external potential, hence, the entire Hamiltonian.

Turning to the second theorem we employ the fact that, by virtue of the variational principle, the energy functional written in terms of a trial wave function $|\Psi\rangle$ assumes its minimum at the correct ground state wave function $|\Psi_0\rangle$, hence

$$\begin{aligned} E[\rho] &= \langle \Psi | H_0 | \Psi \rangle \\ &= F[\rho] + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \\ &\geq F[\rho_0] + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho_0(\mathbf{r}) \\ &= \langle \Psi_0 | H_0 | \Psi_0 \rangle \\ &= E[\rho_0] \quad , \end{aligned} \quad (9.1.27)$$

where the equality holds only if the wave function $|\Psi\rangle$ is identical to the ground state wave function $|\Psi_0\rangle$. Again, we mention the important implications this theorem has for implementing density functional theory as a practical tool.

Together, both theorems represent a great achievement by taking the burden away from evaluating the ground state wave function and using the electron density instead, while the wave function enters only as a vehicle for calculating functionals of the type (9.1.26). The idea underlying DFT thus is the same as in Thomas-Fermi theory, which usually is regarded as the first realization of density functional theory. However, in making the density dependence of the energy functional explicit Thomas-Fermi theory applied to crude an approximation especially to the kinetic energy, which fact caused various deficiencies as

the missing shell structure of atoms or the non-binding property of molecules. It is the merit of Kohn and Sham to resolve the problem in a very elegant manner. In Sec. 9.4 we will see how they succeeded.

9.2 Degenerate ground states

As already pointed out in the preceding section DFT as originally formulated by Hohenberg, Kohn, and Sham was limited to non-degenerate ground states. However, extension to degenerate ground states is readily accomplished as was demonstrated by Kohn [88]. Let us have a closer look at the maps contained in the relation (9.1.25). Now, given an external potential $v_{ext}(\mathbf{r})$, we obtain a set $D(v_{ext})$ of q degenerate ground states all growing out of Schrödinger's equation

$$\begin{aligned} H_0|\Psi_{0i}\rangle &= (H_{el,kin} + H_{el-el} + H_{ext})|\Psi_{0i}\rangle \\ &= E_0|\Psi_{0i}\rangle \quad , \\ &\quad \forall i = 1, \dots, q, \quad |\Psi_{0i}\rangle \in D(v_{ext}) \quad . \end{aligned} \quad (9.2.1)$$

Note that, in contrast to the situation considered in the previous section, the relation between external potentials and ground state wave functions is no longer a map for degenerate ground states, since the external potential may give rise to more than one wave function. Yet, proceeding along the same lines as in the proofs given in Sec. 9.1, Eqs. (9.1.21) to (9.1.24), we realize that two sets $D(v_{ext})$ and $D(v'_{ext})$ are disjoint unless the two external potentials v_{ext} and v'_{ext} differ only by a trivial constant. As a consequence, the relation between (degenerate) ground state wave functions and the external potential is a proper map and we are able to note

$$v_{ext}(\mathbf{r}) \xleftarrow{(1)} |\Psi_{0i}\rangle, \quad \forall i = 1, \dots, q \quad . \quad (9.2.2)$$

Next, each of the degenerate ground state wave functions gives rise to an electron density

$$|\Psi_{0i}\rangle \xrightarrow{(2)} \rho_{0i}(\mathbf{r}), \quad \forall i = 1, \dots, q \quad . \quad (9.2.3)$$

Again employing the same arguments as in Sec. 9.1, Eqs. (9.1.17) to (9.1.20), we can show that two ground states $|\Psi_{0i}\rangle$ and $|\Psi'_{0j}\rangle$ belonging to different sets $D(v_{ext})$ and $D(v'_{ext})$ lead to different densities $\rho_{0i}(\mathbf{r})$ and $\rho'_{0j}(\mathbf{r})$ and, hence, the corresponding subsets grouping the densities are likewise disjoint. Combining this result with Eqs. (9.2.2) and (9.2.3) we may thus write

$$v_{ext}(\mathbf{r}) \xleftarrow{(1)} |\Psi_{0i}\rangle \xleftrightarrow{(2)} \rho_{0i}(\mathbf{r}), \quad \forall i = 1, \dots, q \quad . \quad (9.2.4)$$

This relation is the counterpart of Eq. (9.1.25) for degenerate ground states. To conclude, again we obtain a map from ground state densities to wave functions and external potentials and the first theorem of Hohenberg and Kohn remains in force.

Still we have to take special care of the particular situation, where two different degenerate ground state wave functions lead to identical electronic densities, i.e.

$$v_{ext}(\mathbf{r}) \begin{cases} \nearrow \\ \searrow \end{cases} \begin{matrix} |\Psi_{0i}\rangle \\ |\Psi_{0j}\rangle \end{matrix} \begin{cases} \searrow \\ \nearrow \end{cases} \rho_{0i}(\mathbf{r}) = \rho_{0j}(\mathbf{r}) \quad . \quad (9.2.5)$$

In this case the relation (2) of Eq. (9.2.4) is not a unique map and the ground state expectation value (9.1.26) may no longer be a unique functional of the density. As a consequence, we might thus face problems in setting up the variational principle. However, the energy functional is exceptional in this respect since it is indeed uniquely defined by Schrödinger's equation (9.2.1) or equivalently by

$$\langle \Psi_{0i} | H_0 | \Psi_{0i} \rangle = E_0 \quad , \quad \forall i = 1, \dots, q \quad . \quad (9.2.6)$$

irrespective of the particular choice of the wave function $|\Psi_{0i}\rangle \in D(v_{ext})$. In summary, we are again able to formulate the variational principle with respect to the electronic density.

To conclude, also for a degenerate ground state the external potential is completely determined by the electronic ground state density and so is the Hamiltonian. As before, we are thus able to state that the expectation value of any variable can be equally well expressed in terms of the ground state density instead of the ground state wave function(s). However, this is exactly the content of the theorems by Hohenberg and Kohn.

9.3 Constrained search formulation

Apart from the limitation to non-degenerate ground states the basic theorems given by Hohenberg and Kohn still suffer from a more subtle and at the same time more serious restriction. As outlined in detail in the preceding section the main issue of Hohenberg and Kohn was to revert the relationship between external potential and electron density in order to allow for a complete description of the ground state in terms of the latter. However, by construction, the theorems are valid only for so-called v -representable electronic densities, where

an electronic density is called v -representable if it grows out of the ground state wave function arising from a Hamiltonian (9.1.1) – (9.1.4) with some external potential $v_{ext}(\mathbf{r})$.

In other words, a v -representable density fulfils both relations (1) and (2) of Eq. (9.1.16). From this definition several questions arise immediately, which together constitute what goes under the name v -representability problem.

1. Given the electronic density $\rho(\mathbf{r})$ of an N -electron system, can we always find a local external potential $v_{ext}(\mathbf{r})$, which via a possibly degenerate ground state wave function creates this density?

2. If not, can we extend the validity of the theorems by Hohenberg and Kohn to non v -representable densities?
3. Can we formulate criteria for v -representability?

Of course, we might argue that the possible occurrence of non- v -representable electron densities is outside the realm of the theorems by Hohenberg and Kohn, which were formulated for ground state, hence, physically reasonable, electronic densities, and thus represents a rather academic issue. Nevertheless, in exploiting the variational principle for the energy functional we successively scan the space of all trial densities and, provided non- v -representable densities exist, might easily come across such densities. In such cases we need a way out in order to proceed towards the ground state.

Although Hohenberg and Kohn pointed out that nearly uniform densities are indeed v -representable they were not able to prove this property for arbitrary densities. Lateron, Levy and Lieb demonstrated that the density

$$\rho_0(\mathbf{r}) = \text{tr}(\hat{D}\hat{\rho}(\mathbf{r})) = \sum_{i=1}^q d_i \rho_{0i}(\mathbf{r}) \quad (9.3.1)$$

arising from the density matrix

$$\hat{D} = \sum_{i=1}^q d_i |\psi_{0i}\rangle\langle\psi_{0i}| \quad (9.3.2)$$

of a set of q degenerate ground states $|\psi_{0i}\rangle$ with

$$d_i = d_i^* > 0, \quad \sum_{i=1}^q d_i = 1 \quad , \quad (9.3.3)$$

hence,

$$\rho_{0i}(\mathbf{r}) = \langle\psi_{0i}|\hat{\rho}(\mathbf{r})|\psi_{0i}\rangle \quad (9.3.4)$$

can in general not be derived from a single ground state [102, 104]. However, since the density $\rho_0(\mathbf{r})$ still can be associated with the same external potential as the densities $\rho_{0i}(\mathbf{r})$, the above definition of v -representability was generalized to so-called ensemble v -representability covering densities of the type given by Eq. (9.3.1) and the universal functional $F[\rho]$ extended to mixed states (9.3.2), this laying ground for the so-called ensemble state density functional theory. In contrast, densities, which grow out of a single wave function, were termed pure-state v -representable.

Nevertheless, even this generalization of DFT does not guarantee that an arbitrary “well behaved” density is v -representable. Several examples of non- v -representable densities were given by Englisch and Englisch, who proved that already for a single particle in one dimension densities, which for $x \rightarrow 0$ behave like

$$\rho(x) = \left(a + b|x|^{\alpha+1/2}\right)^2 \quad \text{with } a, b > 0, \quad 0 \leq \alpha < \frac{1}{2} \quad (9.3.5)$$

can not be obtained from an external potential [40].

Having denied the first of the above questions we are left with the hope that the remaining two questions find a positive answer. This is indeed the case. Let us start out from defining a different set of so-called N -representable densities by noting that

an electronic density is called N -representable if it can be obtained from some antisymmetric N -particle wave function.

In contrast to v -representable densities an N -representable density thus has to fulfil only the relation (2) of Eq. (9.1.16). In other words, N -representability is a necessary prerequisite for v -representability and for this reason the set of all N -representable densities comprises that of the v -representable densities.

Fortunately, rigorous conditions for a density to be N -representable exist. To be specific, a density $\rho(\mathbf{r})$ is N -representable if

$$\rho(\mathbf{r}) \geq 0 \quad , \quad (9.3.6)$$

$$\int d^3\mathbf{r} \rho(\mathbf{r}) = N \quad , \quad (9.3.7)$$

$$\int d^3\mathbf{r} |\nabla \sqrt{\rho(\mathbf{r})}|^2 < \infty \quad , \quad (9.3.8)$$

as was shown by Gilbert and subsequently by Lieb [59, 104].

Still, in order to give a positive answer to the last two questions above, it remains to be proven that N -representability constitutes a proper extension of v -representability if used with the theorems by Hohenberg and Kohn. Substantial progress in this respect is due to the constrained search formulation of the variational principle as proposed by Levy and lateron further investigated by Levy and Lieb [101, 102, 104]. Levy started out defining for a given N -representable density $\rho(\mathbf{r})$ a set $S(\rho)$ comprising all those wave functions Ψ , which lead to exactly this density $\rho(\mathbf{r})$. Furthermore he replaced the definition Eq. (9.1.14) of the universal functional by

$$F_{LL}[\rho] = \inf_{|\Psi\rangle \in S(\rho)} \langle \Psi | H_{el,kin}(\{\mathbf{r}_i\}) + H_{el-el}(\{\mathbf{r}_i\}) | \Psi \rangle \quad . \quad (9.3.9)$$

As was demonstrated by Lieb the infimum is actually a minimum [104]. Hence, while for non-degenerate states the set $S(\rho)$ comprises only a single wave function, in case of degeneracies we select that particular wave function in the set $S(\rho)$, which minimizes the expectation value of $H_{el,kin} + H_{el-el}$, the result being $F_{LL}[\rho]$ as given by Eq. (9.3.9). The construction by Levy thus implicitly solves the problem of finding the wave function given an electronic density. Note that the definition (9.3.9) of the Levy functional is not at all restricted to ground state densities but holds for any N -representable density.

Nevertheless, in case $\rho(\mathbf{r})$ denotes a v -representable ground state density, Eq. (9.3.9) via the variational principle leads immediately to the identity

$$F_{LL}[\rho] = F_{HK}[\rho] \quad , \quad (9.3.10)$$

where $F_{HK}[\rho]$ is the functional defined by Hohenberg and Kohn, Eq. (9.1.14). As a consequence $F_{LL}[\rho]$ generalizes the functional $F_{HK}[\rho]$. In order to study the variational properties of the Levy functional $F_{LL}[\rho]$ we minimize the total energy functional

$$E[\rho] = F_{LL}[\rho] + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \quad . \quad (9.3.11)$$

Employing the variational principle in terms of the wave function and using the definition (9.3.9) we note

$$\begin{aligned} E_0[\rho] &= \inf_{|\Psi\rangle} \langle \Psi | H_0 | \Psi \rangle \\ &= \inf_{|\Psi\rangle} \langle \Psi | H_{el,kin} + H_{el-el} + H_{ext} | \Psi \rangle \\ &= \inf_{\rho(\mathbf{r})} \left[\inf_{|\Psi\rangle \in S(\rho)} \langle \Psi | H_{el,kin} + H_{el-el} | \Psi \rangle + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \right] \\ &= \inf_{\rho(\mathbf{r})} \left[F_{LL}[\rho] + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \right] \quad . \end{aligned} \quad (9.3.12)$$

This is the constrained search formulation of the energy functional. Starting from the variational principle for the total energy in terms of the wave functions we perform an unconstrained minimization including all possible wave functions. Splitting this minimization process into two, namely a minimization with respect to the electronic densities and, in addition, for each ρ a constrained minimization within the space $S(\rho)$ containing only those wave functions, which lead to ρ , and finally using the fact that the functional (9.1.15) deriving from the external potential comprises the density instead of the wave function, we arrived at the most natural definition of the universal functional $F_{LL}[\rho]$.

To conclude, the Levy functional (9.3.9) trivially leads to the ground state as well as to the ground state energy. It establishes a variational principle in terms of the density (2nd theorem of Hohenberg and Kohn) and it lets one determine also the external potential solely in terms of the density (1st theorem).

Although density functional theory as outlined so far constitutes a profound basis we are still at a very early stage and have not even exploited the variational principle grounded on the second theorem above. Of course, this step requires some knowledge about the universal functional $F_{LL}[\rho]$. If we knew this functional exactly the Euler-Lagrange equation resulting from the variational principle could be solved and all ground state quantities calculated. However, knowledge about $F_{LL}[\rho]$ is poor and actually most of today's work on density functional theory centers about the issue of improving the approximations used so far for this functional.

In order to define the problems more clearly we start out from Eq. (9.3.9) and, following the original work by Hohenberg and Kohn, write the functional explicitly as

$$F_{LL}[\rho]$$

$$\begin{aligned}
&= \langle \Psi_0 | H_{el,kin}(\{\mathbf{r}_i\}) + H_{el-el}(\{\mathbf{r}_i\}) | \Psi_0 \rangle \\
&= \sum_{\sigma} \int d^3\mathbf{r} \left\{ \frac{\hbar^2}{2m} \langle \Psi_0 | [\nabla\psi_{\sigma}^+(\mathbf{r})] \cdot [\nabla\psi_{\sigma}(\mathbf{r})] | \Psi_0 \rangle \right\} + W_c[\rho] \\
&\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \langle \Psi_0 | \psi_{\sigma}^+(\mathbf{r}) \psi_{\sigma'}^+(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_{\sigma'}(\mathbf{r}') \psi_{\sigma}(\mathbf{r}) | \Psi_0 \rangle \\
&= \frac{\hbar^2}{2m} \sum_{\sigma} \int d^3\mathbf{r} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}', \sigma=\sigma'} \\
&\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{P_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + W_c[\rho] \\
&= \frac{\hbar^2}{2m} \sum_{\sigma} \int d^3\mathbf{r} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}', \sigma=\sigma'} \\
&\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{|\rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} + W_c[\rho] \quad , \tag{9.3.13}
\end{aligned}$$

where $|\Psi_0\rangle$ denotes that particular wave function, which minimizes the Levy-Lieb functional (9.3.9). In addition, we have used the identities (5.7.15) and (5.7.17) for the spin dependent density matrix as well as Eqs. (5.7.23) and (5.7.26). Finally, we have added a so far unknown functional $W_c[\rho]$. It accounts for all those contributions from the electron-electron interaction, which are not covered by the Hartree or exchange term.

As a result we have thus separated out from the universal functional $F_{LL}[\rho]$ the energy due to the classical Coulomb interaction between the electrons. Usually, this step is made explicit by writing the functional as

$$F_{LL}[\rho] = G[\rho] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad , \tag{9.3.14}$$

where

$$\begin{aligned}
G[\rho] &= \frac{\hbar^2}{2m} \sum_{\sigma} \int d^3\mathbf{r} \nabla_{\mathbf{r}} \nabla_{\mathbf{r}'} \rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}', \sigma=\sigma'} \\
&\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{|\rho_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \\
&=: T[\rho] + W_{xc}[\rho] \tag{9.3.15}
\end{aligned}$$

comprises the kinetic as well as the so-called exchange-correlation energy. Here we have implicitly absorbed the function $W_c[\rho]$ used above into the functional $W_{xc}[\rho]$. Note that in the general case of an interacting electron system *both* the energy contributions $T[\rho]$ and $W_{xc}[\rho]$ are not known at all. In contrast, the energy functional (9.1.15) due to the external potential and the Hartree energy,

i.e. the second term on the right hand side of Eq. (9.3.14) can be calculated exactly. To conclude, further work has to concentrate on the functionals $T[\rho]$ and $W_{xc}[\rho]$, which await an explicit evaluation. However, as we shall see in the following sections this goal can be achieved only in an approximate manner.

9.4 The Kohn-Sham equations

Although the basic theorems of density functional theory are stated now, we still need a key to its implementation. Such a key was given shortly after the pioneering work by Hohenberg and Kohn by Kohn and Sham, who exploited the variational principle for the energy functional as implied by the second theorem to derive a set of effective single-particle equations [91].

In order to employ the variational principle we start out again from the representation (9.3.13) to (9.3.15) of the universal functional and insert it into the energy functional (9.3.12), this resulting in

$$\begin{aligned}
E[\rho] &= F_{LL}[\rho] + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \\
&= G[\rho] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&\quad + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \\
&= T[\rho] + W_{xc}[\rho] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&\quad + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \quad .
\end{aligned} \tag{9.4.1}$$

Taking into account particle conservation as formulated in Eq. (9.1.10) we write down the variational principle as

$$\delta \left(E[\rho] - \mu \int d^3\mathbf{r} \rho(\mathbf{r}) \right) \stackrel{!}{=} 0 \quad , \tag{9.4.2}$$

where the Lagrange multiplier μ is identical to the chemical potential, and, combining Eqs. (9.4.1) and (9.4.2), we thus arrive at the Euler-Lagrange equation

$$\begin{aligned}
\frac{\delta E[\rho]}{\delta\rho} - \mu &= \frac{\delta F_{LL}[\rho]}{\delta\rho} + v_{ext}(\mathbf{r}) - \mu \\
&= \frac{\delta G[\rho]}{\delta\rho} + v_H(\mathbf{r}) + v_{ext}(\mathbf{r}) - \mu \\
&= \frac{\delta T[\rho]}{\delta\rho} + \frac{\delta W_{xc}[\rho]}{\delta\rho} + v_H(\mathbf{r}) + v_{ext}(\mathbf{r}) - \mu \\
&\stackrel{!}{=} 0 \quad ,
\end{aligned} \tag{9.4.3}$$

with the Hartree potential given by

$$v_H(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} . \quad (9.4.4)$$

So far, all the steps taken are quite similar to the treatment within Thomas-Fermi-Dirac theory. Nevertheless, as in Chap. 8 we are faced with the problem that the functional $G[\rho]$ comprising the kinetic and exchange-correlation functional is not known at all. As we have learned in Secs. 8.1 and 8.2, Thomas-Fermi-Dirac theory, while neglecting the correlations, approximated the kinetic and exchange energy by the respective expressions derived for the homogeneous electron gas. These were then generalized to arbitrary, varying densities, this leading to the Eqs. (8.1.4) and (8.2.9). As a consequence, a theory evolved, which, despite its remarkable simplicity, allowed to deal with complex atomic aggregates. Yet, as we have learned in Chap. 8, especially the representation of the kinetic energy functional in terms of the electronic density led to severe deficiencies of Thomas-Fermi theory and, hence, undermined its acceptance.

This is where the work by Kohn and Sham sets in, which consists mainly of two important steps,

1. the single-particle wave functions were reintroduced into the formalism,
2. the splitting of the functional $G[\rho]$ into two contributions was performed in a different way as before.

Since, according to the experience with Thomas-Fermi theory, the serious problems in determining the total energy functional center about the kinetic energy contribution let us for a moment reconsider the homogeneous electron gas but ignore the electron-electron interactions. This brings us back to the Sommerfeld model. The important point to notice now is that there exist two different ways to solve the Sommerfeld model exactly. The first one, which we have considered in Sec. 3.1, is built on the (constant) electron density. This approach was later on adopted by Thomas-Fermi theory with the well-know problems. To the contrary, the second way of solving the Sommerfeld model starts from single-particle states, which obviously are plane waves. We have used this approach for treating the homogeneous electron gas in Secs. 7.2 and 7.3. To summarize, the Sommerfeld model could be equally well treated in terms of the density or in terms of single-particle orbitals. Both approaches allow for an exact treatment of this simple model but lead to considerable differences, when applied to inhomogeneous, interacting electron systems. While Thomas and Fermi aimed at an explicit use of the electron density alone, Kohn and Sham opted for the solution in terms of the single-particle orbitals. It was this different strategy, which laid the basis for their success.

In order to make the previous remarks more explicit as well as for pedagogical reasons we concentrate for the time being on the interaction-free N -particle system, where the full Hamiltonian consists only of the single-particle term

(9.1.5). In this case the functionals $F_{LL}[\rho]$ and $G[\rho]$ both reduce to the kinetic energy,

$$F_{LL}[\rho] = G[\rho] = T_s[\rho] \quad . \quad (9.4.5)$$

From this we obtain the total energy functional simply by adding the contribution arising from the external potential according to Eq. (9.4.1). Note that, following convention, we appended the subscript s to the kinetic energy functional in Eq. (9.4.5) indicating the independent-electron case.

In addition, as was already outlined in Sec. 4.1, neglect of the electron-electron interaction allows to write the Hamiltonian as a sum of single-particle Hamiltonians of the form (5.4.13)

$$H_0^{\{1\}} = \sum_{\alpha\beta} \langle \chi_\alpha | \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}^s(\mathbf{r}) \right\} | \chi_\beta \rangle a_\alpha^\dagger a_\beta \quad , \quad (9.4.6)$$

with the single-particle states $|\chi_\alpha\rangle$ growing out of Schrödinger's equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}^s(\mathbf{r}) \right] |\chi_\alpha\rangle = \varepsilon_\alpha |\chi_\alpha\rangle \quad , \quad (9.4.7)$$

which in real space representation reads as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}^s(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) = \varepsilon_\alpha \chi_{\alpha;\sigma}(\mathbf{r}) \quad . \quad (9.4.8)$$

We have used the superscript s to the external potential to indicate that this potential might be of a more general form as just the potential arising from the ions. As usual, we assume the single-particle wave functions, which all grow out of the same Schrödinger equation, to be orthonormalized according to

$$\sum_\sigma \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\beta;\sigma}(\mathbf{r}) = \delta_{\alpha\beta} \quad . \quad (9.4.9)$$

Finally, the many-body wave function is constructed from these single-particle orbitals as a Slater determinant.

The energy functional arises from Eqs. (9.4.6), (5.5.1), (5.5.7), and (5.5.11) as

$$\begin{aligned} E[\rho] &= \langle H_0^{\{1\}} \rangle \\ &= \sum_\alpha \langle \chi_\alpha | \left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{ext}^s(\mathbf{r}) \right\} | \chi_\alpha \rangle n_\alpha \\ &= \sum_\alpha \varepsilon_\alpha n_\alpha \\ &= \sum_\sigma \sum_\alpha \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}^s(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) n_\alpha \\ &= \sum_\sigma \sum_\alpha \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) n_\alpha \\ &\quad + \int d^3\mathbf{r} v_{ext}^s(\mathbf{r}) \rho(\mathbf{r}) \quad , \quad (9.4.10) \end{aligned}$$

where we have turned to the real space representation and used Eq. (9.1.8) for the electronic density. In particular, for the ground state the occupation numbers n_α of the single-particle states reduce to one and zero, respectively, hence, the electronic density reduces to Eq. (9.1.9),

$$\rho_0(\mathbf{r}) = \sum_{\sigma} \sum_{\alpha}^{occ} |\chi_{\alpha;\sigma}(\mathbf{r})|^2 \quad , \quad (9.4.11)$$

and we obtain

$$E[\rho_0] = T_s[\rho_0] + \int d^3\mathbf{r} v_{ext}^s(\mathbf{r})\rho_0(\mathbf{r}) = \sum_{\alpha} \varepsilon_{\alpha} \quad , \quad (9.4.12)$$

where

$$T_s[\rho_0] = \sum_{\sigma} \sum_{\alpha}^{occ} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) \quad (9.4.13)$$

is the ground state kinetic energy functional for non-interacting particles.

In preparing for the second “trick” of Kohn and Sham and being a bit formal we explicitly write down the Euler-Lagrange equations growing out of the energy functional (9.4.12)/(9.4.13) for non-interacting particles, both in terms of the density and the single-particle orbitals, as

$$\frac{\delta E[\rho]}{\delta \rho} - \mu = \frac{\delta T_s[\rho]}{\delta \rho} + v_{ext}^s(\mathbf{r}) - \mu \stackrel{!}{=} 0 \quad (9.4.14)$$

and

$$\frac{\delta E[\rho]}{\delta \chi_{\alpha;\sigma}^*(\mathbf{r})} - \varepsilon_{\alpha} \chi_{\alpha;\sigma}(\mathbf{r}) = \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}^s(\mathbf{r}) - \varepsilon_{\alpha} \right] \chi_{\alpha;\sigma}(\mathbf{r}) \stackrel{!}{=} 0 \quad , \quad (9.4.15)$$

where the Lagrange parameters μ and ε_{α} ensure conservation of the total electron number (9.1.10) as well as of the orthonormalization (9.4.9) of the single-particle orbitals, respectively. Note furthermore the identity with Eqs. (9.4.3) and Schrödinger’s equation (9.4.8).

By introducing an orbital picture we have thus, eventually, arrived at a much improved representation of the kinetic energy, which for an inhomogeneous system of non-interacting particles is exact, hence, superior to Thomas-Fermi theory. As a consequence, already in this rather simple case the approach built on single-particle orbitals is superior to the density approach. Nevertheless, we are still left with the crucial question, how the kinetic energy of an interacting electron system can be handled. As already mentioned above, the central quantity of interest is the universal functional $G[\rho]$, which still awaits its evaluation. This is where the second important step taken by Kohn and Sham comes in. To be specific, they proposed that the splitting of $G[\rho]$ according to Eq. (9.3.15) into the two unknown functionals $T[\rho]$ and $W_{xc}[\rho]$ should be replaced by

$$T[\rho] + W_{xc}[\rho] = G[\rho] \stackrel{!}{=} T_s[\rho] + E_{xc}[\rho] \quad , \quad (9.4.16)$$

where $T_s[\rho]$ is the kinetic energy functional (9.4.13). With this splitting of the universal functional $G[\rho]$ and using Eqs. (9.3.11), (9.3.14), and (9.3.15) we write the energy functional as

$$\begin{aligned}
E[\rho] &= T_s[\rho] + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \\
&\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_\sigma(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho] \\
&= \sum_{\sigma} \sum_{\alpha}^{occ} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \\
&\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_\sigma(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{xc}[\rho] \quad . \quad (9.4.17)
\end{aligned}$$

From this we readily derive the Euler-Lagrange equations as

$$\begin{aligned}
\frac{\delta E[\rho]}{\delta \rho} - \mu &= \frac{\delta T_s[\rho]}{\delta \rho} + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) - \mu \\
&= \frac{\delta T_s[\rho]}{\delta \rho} + v_{eff}(\mathbf{r}) - \mu \stackrel{!}{=} 0 \quad (9.4.18)
\end{aligned}$$

and

$$\begin{aligned}
\frac{\delta E[\rho]}{\delta \chi_{\alpha;\sigma}^*(\mathbf{r})} - \varepsilon_\alpha \chi_{\alpha;\sigma}(\mathbf{r}) \\
&= \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) - \varepsilon_\alpha \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
&= \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}) - \varepsilon_\alpha \right] \chi_{\alpha;\sigma}(\mathbf{r}) \stackrel{!}{=} 0 \quad , \quad (9.4.19)
\end{aligned}$$

where we have defined the exchange-correlation potential

$$v_{xc}(\mathbf{r}) := \frac{\delta E_{xc}[\rho]}{\delta \rho} \quad (9.4.20)$$

and where, as before, the Lagrange parameters μ and ε_α ensure conservation of the total electron number (9.1.10) as well as of the orthonormalization (9.4.9) of the single-particle orbitals, respectively.

The important observation made by Kohn and Sham is that the Euler-Lagrange equations (9.4.14) and (9.4.15) for non-interacting particles are formally identical to the corresponding Eqs. (9.4.18) and (9.4.19) for interacting particles the only difference being that the external potential $v_{ext}^s(\mathbf{r})$ has been replaced by an effective potential

$$v_{eff}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad , \quad (9.4.21)$$

which, in addition to the external potential, contains the Hartree as well as the exchange-correlation potential (9.4.20). As a consequence, the Euler-Lagrange

equation (9.4.19) assumes the form of an effective single-particle Schrödinger equation, which is called the Kohn-Sham equation. Note that the effective potential (9.4.21) via Eqs. (9.4.4) and (9.4.20) still contains the electronic charge density and we are thus, as in the case of the Hartree or Hartree-Fock equations, left with a self-consistent field procedure.

To conclude, by splitting the universal functional $G[\rho]$ into the kinetic energy of a fictitious, non-interacting electron system and a still unknown remainder, which contains part of the kinetic energy of the fully interacting electron system, Kohn and Sham were able to exactly map the complicated many-body problem onto an effective single-particle problem. This way they were able to treat large part of the kinetic energy exactly. However, note that the full many-body wave function remains completely unspecified and even the single-particle states growing out of the Kohn-Sham equation (9.4.19) lack a physical meaning. The same holds true for the “single-particle energies” ε_α , which are just Lagrange-multipliers. As we will learn in Sec. 9.5 below, the energy of the highest occupied level is an exception, since it can be shown to equal the chemical potential μ . Only in the case of non-interacting electrons the physical interpretation of both the single-particle orbitals and energies is restored.

Yet, having derived the Kohn-Sham equations we may still ask, whether there exists a fundamental justification. In particular, it is not at all obvious that there exists a set of single-particle orbitals, which solve the Kohn-Sham equations and give rise to the correct energy functional. In other words, it is not guaranteed that any density ρ is non-interacting v representable, i.e. that a potential v_{ext}^s exists, which gives rise to the correct single-particle states. In order to prove this we follow again the constrained search formulation invented by Levy and use it to express the non-interacting kinetic energy functional

$$\begin{aligned}
 F_{LL,s}[\rho] &= T_s[\rho] \\
 &= \inf_{|\Psi_D\rangle \rightarrow \rho} \langle \Psi_D | H_{el,kin} | \Psi_D \rangle \\
 &= \sum_{\sigma\alpha} \inf_{|\chi_{\alpha;\sigma}|^2 = \rho} \left[\sum_{\sigma} \sum_{\alpha} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) \right] .
 \end{aligned} \tag{9.4.22}$$

Here the search for the infimum was restricted to all those wave functions Ψ_D , which can be written as a single Slater-determinant. To conclude, we may use the same arguments as in Sec. 9.3 to uniquely determine the wave function Ψ_D as well as the “external” potential v_{ext}^s from the electron density, the only difference being the single-particle form of the Hamiltonian (9.4.6).

Finally, the total energy functional is easily accessed by multiplying the Kohn-Sham equation (9.4.19) with $\chi_{\alpha;\sigma}^*(\mathbf{r})$, summing over all occupied states α as well as over spins and integrating over all space,

$$T_s[\rho] + \int d^3\mathbf{r} v_{eff}(\mathbf{r})\rho(\mathbf{r}) - \sum_{\alpha} \varepsilon_{\alpha}$$

$$= T_s[\rho] + \int d^3\mathbf{r} [v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})] \rho(\mathbf{r}) - \sum_{\alpha} \varepsilon_{\alpha} = 0 \quad . \quad (9.4.23)$$

Inserting this expression into the total energy functional as given by Eq. (9.4.1), using the definition (9.4.4) and taking into account the alternative splitting (9.4.16) of the universal functional $G[\rho]$ we obtain the result

$$\begin{aligned} E[\rho] &= T_s[\rho] + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r} v_H(\mathbf{r})\rho(\mathbf{r}) + E_{xc}[\rho] \\ &= \sum_{\alpha} \varepsilon_{\alpha} - \frac{1}{2} \int d^3\mathbf{r} v_H(\mathbf{r})\rho(\mathbf{r}) + E_{xc}[\rho] - \int d^3\mathbf{r} v_{xc}(\mathbf{r})\rho(\mathbf{r}) \quad . \end{aligned} \quad (9.4.24)$$

The total energy thus consists of the sum of the eigenvalues and the so called two-electron or “double-counting” terms.

Density functional theory as outlined above provides an efficient scheme to reduce the entire many-body problem to a Schrödinger-like effective single-particle equation, which has proven to give very good agreement of experimental and theoretical results in numerous cases. Nevertheless, taking a closer look we raise the question as to which material properties are accessible at all by electronic structure calculations, which use this formalism. Of course, from the foundations of DFT we expect ground state properties to be well described of which we just mention quantities like the ionic positions, the electronic density or magnetic moments, which can be directly compared to experimental results e.g. from X-ray or neutron diffraction measurements.

As far as excitation processes are concerned the situation is somewhat more complicated. Within the concept of DFT/LDA the single particle energies resulting from the Kohn-Sham equation (9.4.19) from a very formal point of view are not eigenvalues but Lagrange multipliers. They entered the formalism just to ensure charge conservation. Hence these eigenvalues a priori have no physical meaning although in many cases they can indeed be successfully interpreted as single particle energies (see e.g. the discussion in [98] and references therein).

In view of the aforementioned theoretical foundation of DFT/LDA based electronic structure calculations we understand that relating calculated and measured results requires some care as well as knowledge about the limitations of both theoretical approaches and experimental techniques. As the most striking example in this context we refer to the wellknown problem arising from the straightforward comparison of measured energy gaps of semiconductors and insulators to the energy difference between the highest occupied and lowest unoccupied single particle state. Related difficulties might show up in the theoretical description of photoemission experiments where actually the energy difference between the ground state and an excited state of the correlated electronic many body system, hence, the energy of a quasiparticle is measured.

9.5 Janak's theorem

As was mentioned in the previous section the “single-particle energies” ε_α growing out of the Kohn-Sham equation (9.4.18) entered the formalism as Lagrange-multipliers guaranteeing normalization of the single-particle wave functions. As such they have no physical meaning. In particular, they can not be identified with excitation energies. Only in the case of non-interacting electrons a physical interpretation is possible. However, as experience has shown, in very many cases the agreement with excitation energies is surprisingly good and lays ground for a straightforward comparison of the calculated ε_α with the results of e.g. photoemission experiments. Yet, there exist well known exceptions as the heavy fermion systems, which are characterized by effective masses of up to several hundred electron masses. In view of this somewhat contradictory situation it is thus desirable to get more insight into the meaning of the Kohn-Sham energies and single-particle states.

A first clue was given by Janak [82], who aimed at a proper understanding of single-particle excitations within density functional theory. He started out by introducing the concept of fractional occupation numbers and, hence, generalized the expressions (9.4.11) and (9.4.13) to

$$\tilde{\rho}(\mathbf{r}) = \sum_{\sigma} \sum_{\alpha} |\chi_{\alpha;\sigma}(\mathbf{r})|^2 n_{\alpha} \quad (9.5.1)$$

and

$$\tilde{T}_0[\tilde{\rho}] = \sum_{\sigma} \sum_{\alpha} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) n_{\alpha} \quad , \quad (9.5.2)$$

where $n_{\alpha} \in [0, 1]$ denotes the occupation of the single particle state $|\chi_{\alpha}\rangle$. Of course, it is not at all obvious that this generalization leads to an N -representable, let alone, v -representable electron density. A way out of this would be to fix the occupation numbers n_{α} according to Fermi-Dirac statistics, in which case we would arrive at a physically meaningful density.

With the electron density and the kinetic energy functional as given by Eqs. (9.5.1) and (9.5.2) the total energy functional assumes the generalized form

$$\tilde{E}[\tilde{\rho}] = \tilde{T}_0[\tilde{\rho}] + \int d^3\mathbf{r} v_{eff}(\mathbf{r}) \tilde{\rho}(\mathbf{r}) \quad . \quad (9.5.3)$$

We are now able to calculate the change in total energy with respect to change in the orbital occupation, hence, the response of the total energy to (fractional) particle excitation. We note

$$\begin{aligned} \frac{\partial \tilde{E}[\tilde{\rho}]}{\partial n_{\alpha}} &= \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\ &\quad + \sum_{\sigma} \sum_{\beta} n_{\beta} \frac{\partial}{\partial n_{\alpha}} \int d^3\mathbf{r} \chi_{\beta;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\beta;\sigma}(\mathbf{r}) \end{aligned}$$

$$\begin{aligned}
& + \sum_{\sigma} \int d^3\mathbf{r} v_{eff}(\mathbf{r}) \left[|\chi_{\alpha;\sigma}(\mathbf{r})|^2 + \sum_{\beta} n_{\beta} \frac{\partial |\chi_{\beta;\sigma}(\mathbf{r})|^2}{\partial n_{\alpha}} \right] \\
= & \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
& + \sum_{\sigma} \sum_{\beta} n_{\beta} \left[\frac{\partial}{\partial n_{\alpha}} \int d^3\mathbf{r} \chi_{\beta;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\beta;\sigma}(\mathbf{r}) \right. \\
& \quad \left. + \int d^3\mathbf{r} v_{eff}(\mathbf{r}) \frac{\partial |\chi_{\beta;\sigma}(\mathbf{r})|^2}{\partial n_{\alpha}} \right] \\
= & \varepsilon_{\alpha} + \sum_{\sigma} \sum_{\beta} n_{\beta} \int d^3\mathbf{r} \left\{ \frac{\partial \chi_{\beta;\sigma}^*(\mathbf{r})}{\partial n_{\alpha}} \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}) \right] \chi_{\beta;\sigma}(\mathbf{r}) \right. \\
& \quad \left. + \chi_{\beta;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\mathbf{r}) \right] \frac{\partial \chi_{\beta;\sigma}(\mathbf{r})}{\partial n_{\alpha}} \right\} \\
= & \varepsilon_{\alpha} + \sum_{\sigma} \sum_{\beta} n_{\beta} \varepsilon_{\beta} \int d^3\mathbf{r} \frac{\partial |\chi_{\beta;\sigma}(\mathbf{r})|^2}{\partial n_{\alpha}} \\
= & \varepsilon_{\alpha} \quad , \tag{9.5.4}
\end{aligned}$$

where, in the second but last line, we employed the normalization of the single-particle states. The result (9.5.4) usually goes under the name Janak's theorem. It is similar to Koopman's theorem for Hartree-Fock theory. However, while the latter involves the removal or addition of a whole electron we are here concerned with the derivative of the total energy with respect to *fractional* occupations. For this reason we may not readily interpret the ε_{α} as excitation energies.

Yet, a connection to physical properties can be made by relating Janak's theorem to the total energies of an N and $N + 1$ particle system via

$$E_{N+1} - E_N = \int_0^1 \varepsilon_{\alpha}(n) dn \quad , \tag{9.5.5}$$

where α denotes the highest occupied single-particle orbital. On evaluating Eq. (9.5.5) one may approximate the integral by the value $\varepsilon_{\alpha}(n = 1/2)$ and thereby make a close connection to Slater's transition state concept.

In particular for extended systems the change of the single-particle energy $\varepsilon_{\alpha}(n)$ on removal of an electron, i.e. on changing the occupation n of this state is only small and the integral in Eq. (9.5.5) can be exactly calculated, this leading to the result

$$\mu = E_{N+1} - E_N = \varepsilon_{\alpha} \quad . \tag{9.5.6}$$

To conclude, in extended systems the energy of the highest occupied single-particle state is identical to the chemical potential. This finding was later on rigorously proven by Almbladh and von Barth, who demonstrated that the

eigenvalue of the uppermost occupied orbital equals the exact ionization potential [2].

A quite different approach to the same issue was presented by von Barth [14, 15], who considered the homogeneous, interacting electron gas, where the exact excitation energies are generally given by the implicit equation

$$\varepsilon_{\mathbf{k}\sigma}^{ex} = \frac{\hbar^2 \mathbf{k}^2}{2m} + \Sigma(\mathbf{k}, \varepsilon_{\mathbf{k}\sigma}) \quad . \quad (9.5.7)$$

Here $\Sigma(\mathbf{k}, \varepsilon_{\mathbf{k}\sigma})$ denotes the momentum- and energy-dependent complex self energy.

Eq. (9.5.7) is contrasted by the DFT expression

$$\varepsilon_{\mathbf{k}\sigma}^{DFT} = \frac{\hbar^2 \mathbf{k}^2}{2m} + v_{eff,\sigma} \quad , \quad (9.5.8)$$

where, for the homogeneous electron gas the effective potential has reduced to a constant. As a ground state theory, DFT correctly describes the Fermi energy and the effective potential can thus be identified with the electron self energy taken at the Fermi wave vector and energy,

$$\varepsilon_{\mathbf{k}\sigma}^{DFT} = \frac{\hbar^2 \mathbf{k}^2}{2m} + \Sigma(\mathbf{k}_{F\sigma}, E_{F\sigma}) \quad . \quad (9.5.9)$$

Obviously, the difference between the exact excitation energies $\varepsilon_{\mathbf{k}\sigma}^{ex}$ and the single-particle energies $\varepsilon_{\mathbf{k}\sigma}^{DFT}$ raises from zero as one moves away from the Fermi energy.

$$\varepsilon_{\mathbf{k}\sigma}^{ex} - \varepsilon_{\mathbf{k}\sigma}^{DFT} = \Sigma(\mathbf{k}, \varepsilon_{\mathbf{k}\sigma}) - \Sigma(\mathbf{k}_{F\sigma}, E_{F\sigma}) \quad . \quad (9.5.10)$$

However, the energies differ only to the extent that the self energy $\Sigma(\mathbf{k}, \varepsilon_{\mathbf{k}\sigma})$ varies with \mathbf{k} and $\varepsilon_{\mathbf{k}\sigma}$. If these variations are rather small we can expect the single-particle energies as resulting from the DFT to provide a satisfactory description of excitation energies not only in the vicinity of the Fermi energy.

An alternative way of quantifying the deviation of the DFT from the exact result starts out from expanding the self energy $\Sigma(\mathbf{k}, \omega)$ about the Fermi energy and writing the exact excitation energies $\varepsilon_{\mathbf{k}\sigma}^{ex}$ as

$$\begin{aligned} \omega = \omega_F + \frac{\hbar^2(\mathbf{k}^2 - \mathbf{k}_F^2)}{2m} + (\nabla_{\mathbf{k}}\Sigma)_{\mathbf{k}=\mathbf{k}_F}(\mathbf{k} - \mathbf{k}_F) \\ + \left(\frac{\delta\Sigma}{\delta\omega} \right)_{\omega=\omega_F} (\omega - \omega_F) + \dots \quad . \end{aligned} \quad (9.5.11)$$

The requirement that the self energy varies only slowly with \mathbf{k} and ω can now be expressed in terms of the effective mass m^* . In the effective mass approximation Eq. (9.5.11) is contrasted by

$$\omega = \omega_F + \frac{\hbar^2(\mathbf{k}^2 - \mathbf{k}_F^2)}{2m^*} \quad , \quad (9.5.12)$$

which, in combination with Eq. (9.5.11) leads to

$$\frac{m^*}{m} = \frac{1 - (\delta\Sigma/\delta\omega)_{\omega=\omega_{F\sigma}}}{1 + \frac{m}{\hbar^2 k_{F\sigma}} (\nabla_{\mathbf{k}}\Sigma)_{\mathbf{k}=\mathbf{k}_{F\sigma}}} \quad \text{at } \mathbf{k} = \mathbf{k}_{F\sigma} \quad . \quad (9.5.13)$$

For a self energy slowly varying with both \mathbf{k} and ω we thus have the condition $m^*/m \approx 1$, which holds for most of the simple metals but is strongly violated by the heavy fermion compounds. An intermediate situation arises when we aim at the electronic structure far below or above the Fermi energy, where the difference between the exact self energy and its DFT counterpart eventually becomes appreciably.

9.6 Spin-density functional theory

The generalization of density functional theory to spin-polarized systems, already discussed by Kohn and Sham [91], was worked out in detail by von Barth and Hedin, Pant and Rajagopal as well as, for relativistic systems, Rajagopal and Callaway [17, 123, 139].

In general, spin-polarization may arise from a corresponding symmetry breaking contribution to the external potential, specifically an external magnetic field. Nevertheless, it may likewise be the consequence of the electron-electron interaction and then can be traced back to the exchange term. The latter situation has been discussed for the homogeneous electron gas in Sec. 7.3, which for low densities displayed an instability of the spin-degenerate case in favour of full spin-polarization as displayed in Fig. 7.7.

In the presence of an external magnetic field the response of the electrons may be twofold since the field can couple to both the orbital currents and the electron spin. Ignoring for the time being the former coupling, which has been dealt with by Vignale and Rasolt [165, 166], we concentrate especially on the coupling of the electron spin to an external magnetic field. In this case the contribution (9.1.13) to the Hamiltonian referring to the external potential has to be rewritten as

$$H_{ext}(\{\mathbf{r}_i\}) = \int d^3\mathbf{r} [v_{ext}(\mathbf{r})\hat{\rho}(\mathbf{r}) - \mu_B \mathbf{B}(\mathbf{r}) \cdot \hat{\mathbf{m}}(\mathbf{r})] \quad , \quad (9.6.1)$$

where $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton. In addition, we have introduced the vector of the spin density operator

$$\hat{\mathbf{m}}(\mathbf{r}) = - \sum_{\sigma\sigma'} \psi_{\sigma}^+(\mathbf{r}) \boldsymbol{\sigma}_{\sigma\sigma'} \psi_{\sigma'}(\mathbf{r}) \quad , \quad (9.6.2)$$

which generalizes Eq. (5.7.8) and where $\boldsymbol{\sigma}$ denotes the vector of Pauli matrices,

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (9.6.3)$$

Note that the spin density operator (9.6.2) just denotes special linear combinations of the spin density matrices (5.7.15) for equal sites

$$\begin{aligned}\hat{\rho}_{\sigma\sigma'}(\mathbf{r}) &= \hat{\rho}_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')\delta(\mathbf{r} - \mathbf{r}') \\ &= \psi_{\sigma'}^+(\mathbf{r})\psi_{\sigma}(\mathbf{r}) \quad .\end{aligned}\quad (9.6.4)$$

Specifically, we have

$$\hat{\mathbf{m}}(\mathbf{r}) = -\sum_{\sigma\sigma'} \boldsymbol{\sigma}_{\sigma\sigma'} \hat{\rho}_{\sigma'\sigma}(\mathbf{r}) \quad , \quad (9.6.5)$$

$$\hat{m}_x(\mathbf{r}) = -(\hat{\rho}_{\uparrow\downarrow}(\mathbf{r}) + \hat{\rho}_{\downarrow\uparrow}(\mathbf{r})) \quad , \quad (9.6.6)$$

$$\hat{m}_y(\mathbf{r}) = i(\hat{\rho}_{\downarrow\uparrow}(\mathbf{r}) - \hat{\rho}_{\uparrow\downarrow}(\mathbf{r})) \quad , \quad (9.6.7)$$

$$\hat{m}_z(\mathbf{r}) = -(\hat{\rho}_{\uparrow\uparrow}(\mathbf{r}) - \hat{\rho}_{\downarrow\downarrow}(\mathbf{r})) \quad , \quad (9.6.8)$$

which latter is identical to Eq. (5.7.8). Just to be complete we note

$$\begin{aligned}\hat{\rho}(\mathbf{r}) &= \sum_{\sigma} \hat{\rho}_{\sigma}(\mathbf{r}) \\ &= \sum_{\sigma\sigma'} \delta_{\sigma\sigma'} \hat{\rho}_{\sigma'\sigma}(\mathbf{r}) \\ &= \hat{\rho}_{\uparrow\uparrow}(\mathbf{r}) + \hat{\rho}_{\downarrow\downarrow}(\mathbf{r}) \quad ,\end{aligned}\quad (9.6.9)$$

With these identities at hand we cast the contribution (9.6.1) to the Hamiltonian into the compact form

$$H_{ext}(\{\mathbf{r}_i\}) = \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{ext,\sigma\sigma'}(\mathbf{r}) \hat{\rho}_{\sigma'\sigma}(\mathbf{r}) \quad , \quad (9.6.10)$$

where

$$v_{ext,\sigma\sigma'}(\mathbf{r}) = v_{ext}(\mathbf{r})\delta_{\sigma\sigma'} + \mu_B \mathbf{B}(\mathbf{r}) \cdot \boldsymbol{\sigma}_{\sigma\sigma'} \quad . \quad (9.6.11)$$

Finally, we note for the ground state expectation values

$$\rho(\mathbf{r}) = \langle \Psi_0 | \hat{\rho}(\mathbf{r}) | \Psi_0 \rangle \quad , \quad (9.6.12)$$

$$\mathbf{m}(\mathbf{r}) = \langle \Psi_0 | \hat{\mathbf{m}}(\mathbf{r}) | \Psi_0 \rangle \quad , \quad (9.6.13)$$

or, alternatively, the compact variant

$$\begin{aligned}\rho_{\sigma\sigma'}(\mathbf{r}) &= \langle \Psi_0 | \hat{\rho}_{\sigma\sigma'}(\mathbf{r}) | \Psi_0 \rangle \\ &= \langle \Psi_0 | \psi_{\sigma'}^+(\mathbf{r})\psi_{\sigma}(\mathbf{r}) | \Psi_0 \rangle \quad .\end{aligned}\quad (9.6.14)$$

In close analogy to Eq. (9.1.15) the functional arising from the external potential is thus written as

$$\langle \Psi_0 | H_{ext}(\{\mathbf{r}_i\}) | \Psi_0 \rangle = \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{ext,\sigma\sigma'}(\mathbf{r}) \rho_{\sigma'\sigma}(\mathbf{r}) \quad . \quad (9.6.15)$$

In contrast, the expression (9.1.15) for the universal functional $F[\rho]$ remains unaltered with the slight exception that the dependence on the density has to be replaced by the dependence on the spin density matrix.

In order to formulate density functional theory for spin-polarized systems we next have to prove the proper generalization of the theorems by Hohenberg and Kohn. To this end we first investigate the relation

$$|\Psi_0\rangle \xrightarrow{(2)} \rho_{0,\sigma\sigma'}(\mathbf{r}) \quad (9.6.16)$$

between the ground state and its spin density matrix. For a non-degenerate ground state two different wave functions $|\Psi_0\rangle \neq |\Psi'_0\rangle$ then lead to two different spin density matrices $\rho_{0,\sigma\sigma'}(\mathbf{r}) \neq \rho'_{0,\sigma\sigma'}(\mathbf{r})$. Following the proof given in Eqs. (9.1.17) to (9.1.20) but replacing Eq. (9.1.18) by

$$E' = E + \sum_{\sigma\sigma'} \int d^3\mathbf{r} [v'_{ext,\sigma\sigma'}(\mathbf{r}) - v_{ext,\sigma\sigma'}(\mathbf{r})] \rho_{\sigma'\sigma}(\mathbf{r}) \quad (9.6.17)$$

and Eq. (9.1.19) by the analogous expression with primed and unprimed quantities exchanged we are able to prove invertibility of this map also for spin-polarized systems,

$$|\Psi_0\rangle \xleftrightarrow{(2)} \rho_{0,\sigma\sigma'}(\mathbf{r}) \quad . \quad (9.6.18)$$

Again, the constrained search formulation proposed by Levy offers several advantages in setting up the theorems by Hohenberg and Kohn. We thus write instead of Eq. (9.3.12)

$$\begin{aligned} E_0[\rho] &= \inf_{|\Psi\rangle} \langle \Psi | H_0 | \Psi \rangle \\ &= \inf_{|\Psi\rangle} \langle \Psi | H_{el,kin} + H_{el-el} + H_{ext} | \Psi \rangle \\ &= \inf_{\rho_{\sigma\sigma'}(\mathbf{r})} \left[\inf_{|\Psi\rangle \in S(\rho_{\sigma\sigma'})} \langle \Psi | H_{el,kin} + H_{el-el} | \Psi \rangle \right. \\ &\quad \left. + \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{ext,\sigma\sigma'}(\mathbf{r}) \rho_{\sigma'\sigma}(\mathbf{r}) \right] \\ &= \inf_{\rho_{\sigma\sigma'}(\mathbf{r})} \left[F_{LL}[\rho_{\sigma\sigma'}] + \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{ext,\sigma\sigma'}(\mathbf{r}) \rho_{\sigma'\sigma}(\mathbf{r}) \right] \quad (9.6.19) \end{aligned}$$

where the universal functional is explicitly given by

$$F_{LL}[\rho_{\sigma\sigma'}] = \inf_{|\Psi\rangle \in S(\rho_{\sigma\sigma'})} \langle \Psi | H_{el,kin}(\{\mathbf{r}_i\}) + H_{el-el}(\{\mathbf{r}_i\}) | \Psi \rangle \quad (9.6.20)$$

with the set $S(\rho_{\sigma\sigma'})$ now comprising all those wave functions, which lead to the particular spin density matrix $\rho_{\sigma\sigma'}$.

To conclude, also for spin-polarized systems we have succeeded in proving the fundamental theorems, as Eq. (9.6.19) establishes the variational principle in terms of the spin density matrix (2nd theorem) and furthermore provides a means to express the ground state also in terms of this spin density matrix (1st theorem).

However, one ambiguity remains for spin-polarized systems, which has been the matter of long debates and has found a definite answer only recently [37, 26, 43]. It is centered about the relation between external potentials and ground state wave functions, in particular, about the question, if two different external potentials $v'_{ext,\sigma\sigma'} \neq v_{ext,\sigma\sigma'}$ can lead to the same ground state wave function. For non-spin-polarized, non-degenerate ground states this point has been clarified by Eqs. (9.1.21) to (9.1.24). In contrast, for spin-polarized systems, Eq. (9.1.23) writes as

$$\begin{aligned} & [H_{ext} - H'_{ext}] |\Psi_0\rangle \\ &= \sum_{\sigma\sigma'} \int d^3\mathbf{r} [v_{ext,\sigma\sigma'}(\mathbf{r}) - v'_{ext,\sigma\sigma'}(\mathbf{r})] \hat{\rho}_{\sigma'\sigma}(\mathbf{r}) |\Psi_0\rangle \\ &= [E - E'] |\Psi_0\rangle \quad , \end{aligned} \quad (9.6.21)$$

which defines a 2×2 eigenvalue problem

$$\det \{ v_{ext,\sigma\sigma'}(\mathbf{r}) - v'_{ext,\sigma\sigma'}(\mathbf{r}) - (E - E') \delta_{\sigma\sigma'} \} = 0 \quad . \quad (9.6.22)$$

Indeed this can be solved by two potentials differing by more than a constant. However, note that this finding, while violating injectivity of the first map entering Eqs. (9.1.16) and (9.1.25), does not affect the validity of the theorems by Hohenberg and Kohn, as we have just demonstrated by writing the total energy in terms of the Levy-Lieb functional in Eq. (9.6.19). This is due to the fact that the constrained search formulation requires only N -representability of the electronic density whereas the external potential does not enter any of the proofs.

Having laid ground the formal basis of spin-density functional theory we still have to derive the spin-dependent single-particle Kohn-Sham equations. To this end we start out again writing down the complete energy functional, which, except for the inclusion of the term growing out of the magnetic field, is formally identical to Eq. (9.4.17). We write

$$\begin{aligned} E[\rho] &= T_s[\rho] + \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{ext,\sigma\sigma'}(\mathbf{r}) \rho_{\sigma'\sigma}(\mathbf{r}) \\ &\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_\sigma(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho] \\ &= \sum_{\sigma} \sum_{\alpha}^{occ} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\ &\quad + \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{ext,\sigma\sigma'}(\mathbf{r}) \rho_{\sigma'\sigma}(\mathbf{r}) \\ &\quad + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_\sigma(\mathbf{r}) \rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho] \\ &= \sum_{\sigma} \sum_{\alpha}^{occ} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha;\sigma}(\mathbf{r}) \end{aligned}$$

$$\begin{aligned}
& + \sum_{\sigma\sigma'} \sum_{\alpha}^{occ} \int d^3\mathbf{r} v_{ext,\sigma\sigma'}(\mathbf{r}) \chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\alpha;\sigma'}(\mathbf{r}) \\
& + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \sum_{\alpha\beta}^{occ} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{|\chi_{\alpha;\sigma}(\mathbf{r})|^2 |\chi_{\beta;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\rho] \quad .
\end{aligned} \tag{9.6.23}$$

In the last lines we have added a formulation using the explicit expressions (5.7.14) and (5.7.17) of the spin density as well as the spin-dependent density matrix, respectively, in terms of the single-particle orbitals. Using the orthonormalization of these orbitals, we then obtain the Kohn-Sham equations as

$$\begin{aligned}
& \frac{\delta E[\rho]}{\delta \chi_{\alpha;\sigma}^*(\mathbf{r})} - \varepsilon_{\alpha;\sigma} \chi_{\alpha;\sigma}(\mathbf{r}) \\
& = \sum_{\sigma'} \left[-\delta_{\sigma\sigma'} \frac{\hbar^2}{2m} \nabla^2 + v_{ext,\sigma\sigma'}(\mathbf{r}) + \delta_{\sigma\sigma'} v_H(\mathbf{r}) \right. \\
& \qquad \qquad \qquad \left. + v_{xc,\sigma\sigma'}(\mathbf{r}) - \delta_{\sigma\sigma'} \varepsilon_{\alpha;\sigma} \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
& = \left[-\delta_{\sigma\sigma'} \frac{\hbar^2}{2m} \nabla^2 + v_{eff,\sigma\sigma'}(\mathbf{r}) - \delta_{\sigma\sigma'} \varepsilon_{\alpha;\sigma} \right] \chi_{\alpha;\sigma}(\mathbf{r}) \stackrel{!}{=} 0 \quad , \tag{9.6.24}
\end{aligned}$$

where we have used the definition of the Hartree potential

$$\begin{aligned}
v_H(\mathbf{r}) & = \sum_{\sigma'} \int d^3\mathbf{r}' \frac{\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
& = \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad , \tag{9.6.25}
\end{aligned}$$

as well as that of the exchange-correlation potential

$$v_{xc,\sigma\sigma'}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho_{\sigma'\sigma}(\mathbf{r})} \quad . \tag{9.6.26}$$

In addition, we have in the last step of Eq. (9.6.24) implicitly defined the effective potential matrix

$$v_{eff,\sigma\sigma'}(\mathbf{r}) = v_{ext,\sigma\sigma'}(\mathbf{r}) + \delta_{\sigma\sigma'} v_H(\mathbf{r}) + v_{xc,\sigma\sigma'}(\mathbf{r}) \quad . \tag{9.6.27}$$

To conclude, for spin-polarized systems we arrive at a set of two coupled Kohn-Sham equations, one for each spin.

Finally, in order the standard expression of the total energy functional in terms of the single particle energies we multiply the Kohn-Sham equations (9.6.24) with $\chi_{\alpha;\sigma}^*(\mathbf{r})$, sum over all occupied states α as well as both spins and integrate over all space,

$$T_s[\rho] + \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{eff,\sigma\sigma'}(\mathbf{r}) \rho_{\sigma'\sigma}(\mathbf{r}) - \sum_{\sigma} \sum_{\alpha} \varepsilon_{\alpha;\sigma}$$

$$\begin{aligned}
&= T_s[\rho] - \sum_{\sigma} \sum_{\alpha} \varepsilon_{\alpha;\sigma} \\
&\quad + \sum_{\sigma\sigma'} \int d^3\mathbf{r} [v_{ext,\sigma\sigma'}(\mathbf{r}) + \delta_{\sigma\sigma'} v_H(\mathbf{r}) + v_{xc,\sigma\sigma'}(\mathbf{r})] \rho_{\sigma'\sigma}(\mathbf{r}) \\
&= 0 \quad .
\end{aligned} \tag{9.6.28}$$

Inserting this expression into the total energy functional as given by Eq. (9.6.23), using the definition (9.4.4) we obtain the result

$$\begin{aligned}
E[\rho] &= T_s[\rho] + \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{eff,\sigma\sigma'}(\mathbf{r}) \rho_{\sigma'\sigma}(\mathbf{r}) \\
&\quad + \frac{1}{2} \int d^3\mathbf{r} v_H(\mathbf{r}) \rho(\mathbf{r}) + E_{xc}[\rho] \\
&= \sum_{\sigma} \sum_{\alpha} \varepsilon_{\alpha;\sigma} - \frac{1}{2} \int d^3\mathbf{r} v_H(\mathbf{r}) \rho(\mathbf{r}) \\
&\quad + E_{xc}[\rho] - \sum_{\sigma\sigma'} \int d^3\mathbf{r} v_{xc,\sigma\sigma'}(\mathbf{r}) \rho_{\sigma'\sigma}(\mathbf{r}) \quad , \tag{9.6.29}
\end{aligned}$$

which again consists of the sum of the eigenvalues and the so called two-electron or “double-counting” terms.

Chapter 10

Local density approximation and beyond

10.1 Local density approximation

So far our discussion about density functional theory has been of somewhat artificial nature since we have not yet specified the exchange-correlation functional. The missing link is provided by the local density approximation (LDA), which is the subject of the present section.

The starting point for the local density approximation is the expression of the exchange-correlation energy as an integral over the local exchange-correlation energy density weighted with the local electron density,

$$E_{xc}[\rho] = \int d^3\mathbf{r} \rho(\mathbf{r})\epsilon_{xc}(\rho(\mathbf{r})) \quad . \quad (10.1.1)$$

Note that $\epsilon_{xc}(\rho)$ is a function of the density rather than a functional. The energy density in turn is evaluated from the respective expression for the homogeneous, interacting electron gas, where the electron density is a constant in space.

The main idea behind the local density approximation is that for any real system, where of course the density is *not* homogeneous, space may be divided into small “boxes” such that within each box the variation of the density is small. We denote the average density within the box located at \mathbf{r} as $\rho(\mathbf{r})$. If the variation of the density outside a box is ignored but the whole system assumed to behave as a homogeneous electron gas with the density $\rho(\mathbf{r})$ we have a notion to calculate the energy density and the potential within the box and, finally, by combining the results for all the boxes, to arrive at a prescription of the inhomogeneous electron gas as a superposition of locally homogeneous electron gases.

From these considerations it becomes clear that the local density approximation is exact in the limit of a constant density or density matrix, respectively.

In addition, we would expect it to be quite good for slowly varying densities but not for systems as atoms or molecules where the density depends strongly on position. Even for solids the deviation from a homogeneous density is substantial and thus cannot be neglected. Surprisingly, experience shows that the local density approximation works well in a large number of cases.

Using Eq. (9.4.19) we express the exchange-correlation potential in terms of the energy density as

$$\begin{aligned} v_{xc}(\rho(\mathbf{r})) &= \left[\frac{\partial}{\partial \rho} \{ \rho \epsilon_{xc}(\rho) \} \right]_{\rho=\rho(\mathbf{r})} \\ &= \epsilon_{xc}(\rho(\mathbf{r})) + \rho(\mathbf{r}) \left[\frac{\partial}{\partial \rho} \{ \epsilon_{xc}(\rho) \} \right]_{\rho=\rho(\mathbf{r})} . \end{aligned} \quad (10.1.2)$$

For the spin-polarized ground state we have both the spin up and down density at hand, which may be expressed in terms of the density and the spin polarization,

$$\rho(\mathbf{r}) = \rho_{\uparrow}(\mathbf{r}) + \rho_{\downarrow}(\mathbf{r}) \quad , \quad \zeta(\mathbf{r}) = \frac{\rho_{\uparrow}(\mathbf{r}) - \rho_{\downarrow}(\mathbf{r})}{\rho(\mathbf{r})} \quad , \quad (10.1.3)$$

as

$$\rho_{\alpha}(\mathbf{r}) = \frac{\rho(\mathbf{r})}{2} \left(1 + z_{\alpha} \zeta(\mathbf{r}) \right) \quad (10.1.4)$$

where $\alpha = \uparrow, \downarrow$ and

$$z_{\alpha} = \begin{cases} +1 & \text{for } \alpha = \uparrow \\ -1 & \text{for } \alpha = \downarrow \end{cases} . \quad (10.1.5)$$

Even in the general situation described in subsection 9.6, where we lack a global spin quantization axis, the eigenvalues ρ_{\uparrow} and ρ_{\downarrow} of the spin density matrix (9.6.4), hence, the spin-up and spin-down density, are locally well defined. We are thus able to write the exchange-correlation energy and potential as [17, 42]

$$E_{xc}[\rho] = \int d^3\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r}), \zeta(\mathbf{r})) \quad (10.1.6)$$

and

$$v_{xc,\sigma}(\rho(\mathbf{r}), \zeta(\mathbf{r})) = \left[\frac{\partial}{\partial \rho_{\sigma}} \{ \rho \epsilon_{xc}(\rho, \zeta) \} \right]_{\rho=\rho(\mathbf{r}), \zeta=\zeta(\mathbf{r})} . \quad (10.1.7)$$

Using the identity

$$\frac{\partial}{\partial \rho_{\sigma}} = \frac{\partial \rho}{\partial \rho_{\sigma}} \frac{\partial}{\partial \rho} + \frac{\partial \zeta}{\partial \rho_{\sigma}} \frac{\partial}{\partial \zeta} = \frac{\partial}{\partial \rho} + \frac{z_{\sigma} - \zeta}{\rho} \frac{\partial}{\partial \zeta} \quad , \quad (10.1.8)$$

which follows from equation (10.1.3), we may further write

$$v_{xc,\sigma}(\rho(\mathbf{r}), \zeta(\mathbf{r})) = \left[\frac{\partial}{\partial \rho} \{ \rho \epsilon_{xc}(\rho, \zeta) \} + (z_{\sigma} - \zeta) \frac{\partial}{\partial \zeta} \{ \epsilon_{xc}(\rho, \zeta) \} \right]_{\rho=\rho(\mathbf{r}), \zeta=\zeta(\mathbf{r})} . \quad (10.1.9)$$

We have thus reduced the problem of determining the exchange-correlation energy and potential to the problem of expressing the energy density in terms of the charge density and the spin polarization. Nowadays there exist several parametrizations for the energy density, which were derived from perturbation theory or accurate Monte Carlo simulations of the homogeneous electron gas. Following a recent overview by MacLaren *et al.* [108] we will in the remaining part of this section describe some of these schemes in more detail.

Nevertheless, despite a variety of different schemes there exist some more general rules, which are obeyed by most parametrizations. Among these is the so-called RPA scaling proposed by Hedin [74], which relates the energy densities for the non-spin-polarized and the fully polarized ground state by

$$\epsilon_{xc}^{RPA}(\rho, \zeta = 1) = \frac{1}{2} \epsilon_{xc}^{RPA}(2^4 \rho, \zeta = 0) \quad . \quad (10.1.10)$$

Furthermore, von Barth and Hedin proposed to model the polarization dependence of the exchange-correlation energy density of the homogeneous electron gas between the paramagnetic ($\zeta = 0$) and the saturated ferromagnetic ($\zeta = 1$) cases according to the so-called spin interpolation formula,

$$\epsilon_{xc}(\rho, \zeta) = \epsilon_{xc}^P(\rho) + [\epsilon_{xc}^F(\rho) - \epsilon_{xc}^P(\rho)] f(\zeta) \quad , \quad (10.1.11)$$

where

$$\epsilon_{xc}^P(\rho) = \epsilon_{xc}(\rho, \zeta = 0) \quad , \quad (10.1.12)$$

$$\epsilon_{xc}^F(\rho) = \epsilon_{xc}(\rho, \zeta = 1) \quad , \quad (10.1.13)$$

and

$$f(\zeta) = \frac{1}{2^{\frac{4}{3}} - 2} \left[\left(\frac{2\rho_{\uparrow}}{\rho} \right)^{\frac{4}{3}} + \left(\frac{2\rho_{\downarrow}}{\rho} \right)^{\frac{4}{3}} - 2 \right] = \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3} - 2}{2^{\frac{4}{3}} - 2} \quad . \quad (10.1.14)$$

is the spin interpolation function $f(\zeta)$, which is displayed in Fig. 10.1. Obviously, this function is symmetric in ζ and so is the exchange-correlation energy density $\epsilon_{xc}(\rho, \zeta)$. In conclusion, the spin dependence of the energy density and potential is completely determined by equations (10.1.9) to (10.1.14), and, if we are willing to accept the RPA scaling and the spin interpolation formula, we are left with only the problem of evaluating the ρ -dependence of $\epsilon_{xc}^P(\rho)$.

Combining equations (10.1.9) and (10.1.11) we are finally able to derive a spin interpolation formula for the exchange-correlation potential

$$\begin{aligned} v_{xc,\sigma}(\rho, \zeta) &= \frac{\partial}{\partial \rho} \{ \rho \epsilon_{xc}^P(\rho) \} + \left[\frac{\partial}{\partial \rho} \{ \rho \epsilon_{xc}^F(\rho) \} - \frac{\partial}{\partial \rho} \{ \rho \epsilon_{xc}^P(\rho) \} \right] f(\zeta) \\ &\quad + (z_{\sigma} - \zeta) [\epsilon_{xc}^F(\rho) - \epsilon_{xc}^P(\rho)] \frac{\partial}{\partial \zeta} \{ f(\zeta) \} \quad . \quad (10.1.15) \end{aligned}$$

Using the definition

$$\mu_{xc}^i(\rho) := \frac{\partial}{\partial \rho} \{ \rho \epsilon_{xc}^i(\rho) \} = \epsilon_{xc}^i(\rho) + \rho \frac{\partial}{\partial \rho} \epsilon_{xc}^i \quad \text{for } i = P, F \quad (10.1.16)$$

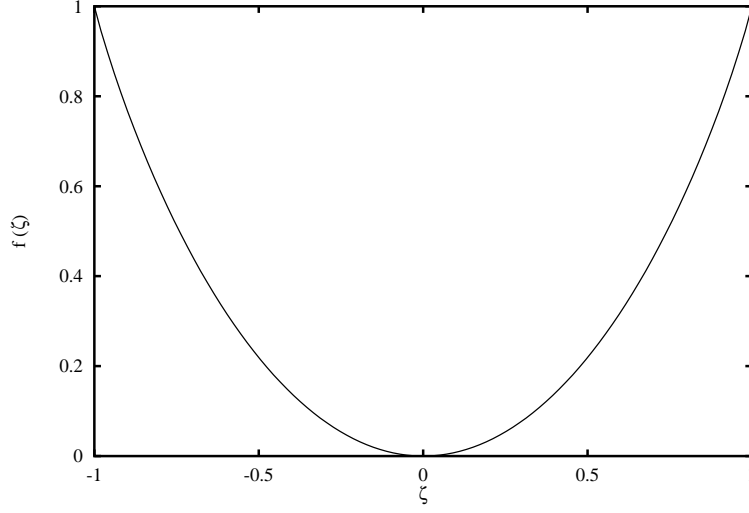


Figure 10.1: Spin polarization interpolation function $f(\zeta)$ as given by equation (10.1.14).

as well as the derivative

$$(z_\sigma - \zeta) \frac{\partial f(\zeta)}{\partial \zeta} = \gamma \left((1 + z_\sigma \zeta)^{\frac{1}{3}} - 1 \right) - \frac{4}{3} f(\zeta) \quad , \quad (10.1.17)$$

where

$$\gamma = \frac{4}{3} \frac{1}{2^{\frac{1}{3}} - 1} \quad (10.1.18)$$

we thus get the result

$$\begin{aligned} v_{xc,\sigma}(\rho, \zeta) &= \mu_{xc}^P(\rho) + [\mu_{xc}^F(\rho) - \mu_{xc}^P(\rho)] f(\zeta) \\ &\quad + [\epsilon_{xc}^F(\rho) - \epsilon_{xc}^P(\rho)] \left[\gamma \left((1 + z_\sigma \zeta)^{\frac{1}{3}} - 1 \right) - \frac{4}{3} f(\zeta) \right] \end{aligned} \quad (10.1.19)$$

for the spin interpolation of the exchange-correlation potential.

The first approach to modelling the energy density and potential goes back to Kohn, Sham and Gaspár (KSG), who ignored any contribution due to correlations and specified the exchange energy density as

$$\epsilon_x^P(\rho) = -\frac{3e^2 k_F}{4\pi} = -\frac{3e^2}{4\pi} (3\pi^2 \rho)^{\frac{1}{3}} \quad , \quad (10.1.20)$$

where k_F is the Fermi wave vector. Following common practice we express the density in terms of the density parameter r_S as

$$\frac{4\pi}{3} r_S^3 = \frac{1}{\rho} \quad . \quad (10.1.21)$$

For later use we note

$$\rho \frac{dr_s}{d\rho} = -\frac{1}{3} \left(\frac{3}{4\pi\rho} \right)^{\frac{1}{3}} = -\frac{1}{3} r_s \quad . \quad (10.1.22)$$

With our choice of atomic units, especially with $e^2 = 2$, we thus obtain

$$\epsilon_x^P(\rho) = -3 \left(\frac{3\rho}{8\pi} \right)^{\frac{1}{3}} = -\frac{\epsilon_x^0}{r_s} \quad , \quad (10.1.23)$$

where we have abbreviated

$$\epsilon_x^0 = \frac{3}{2\pi} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} = 0.916330587 \quad . \quad (10.1.24)$$

The exchange energy density for the ferromagnetically saturated ground state arises from the RPA scaling, equation (10.1.10), as

$$\epsilon_x^F(\rho) = 2^{\frac{1}{3}} \epsilon_x^P(\rho) \quad . \quad (10.1.25)$$

From this we get

$$\epsilon_x^F(\rho) - \epsilon_x^P(\rho) = (2^{\frac{1}{3}} - 1) \epsilon_x^P(\rho) = -(2^{\frac{1}{3}} - 1) \frac{\epsilon_x^0}{r_s} = -0.238173608 \frac{1}{r_s} \quad . \quad (10.1.26)$$

Combining now equations (10.1.11), (10.1.14) and (10.1.26) we obtain the following result for the exchange energy density

$$\begin{aligned} \epsilon_x(\rho, \zeta) &= \epsilon_x^P(\rho) + (2^{\frac{1}{3}} - 1) \epsilon_x^P(\rho) f(\zeta) \\ &= \frac{1}{2} \epsilon_x^P(\rho) \left[\left(\frac{2\rho_{\uparrow}}{\rho} \right)^{\frac{4}{3}} + \left(\frac{2\rho_{\downarrow}}{\rho} \right)^{\frac{4}{3}} \right] \quad . \end{aligned} \quad (10.1.27)$$

In the last line we have added the alternative representation of the spin interpolation function $f(\zeta)$ as a sum over the two spin channels, which was already given in equation (10.1.14). Since, according to equation (10.1.23), the paramagnetic exchange energy density scales as $\rho^{1/3}$, we may further write

$$\rho \epsilon_x(\rho, \zeta) = \frac{1}{2} [2\rho_{\uparrow} \epsilon_x^P(2\rho_{\uparrow}) + 2\rho_{\downarrow} \epsilon_x^P(2\rho_{\downarrow})] \quad , \quad (10.1.28)$$

and inserting this into Eq. (10.1.6) we obtain

$$\begin{aligned} E_x[\rho_{\uparrow}, \rho_{\downarrow}] &= \sum_{\sigma} \int d^3\mathbf{r} \rho_{\sigma}(\mathbf{r}) \epsilon_x^P(2\rho_{\sigma}(\mathbf{r})) \\ &= -\frac{3e^2}{4\pi} (6\pi^2)^{\frac{1}{3}} \sum_{\sigma} \int d^3\mathbf{r} \rho_{\sigma}^{\frac{4}{3}}(\mathbf{r}) \\ &= \frac{1}{2} [E_x[2\rho_{\uparrow}] + E_x[2\rho_{\downarrow}]] \quad . \end{aligned} \quad (10.1.29)$$

We thus arrive at two alternative representation of the density weighted exchange energy density, $\rho\epsilon_x(\rho, \zeta)$, as a single function, which is symmetric with respect to exchange of spin up and down, or as a sum of contributions from both spin directions, which comprises only the *paramagnetic* exchange energy densities. This is where the RPA scaling (10.1.25) comes in again. The second representation of the weighted exchange energy density will be used especially in connection with the generalized gradient approximation to be presented in section 10.3.

From the previous specifications of the energy density we are finally in a position to derive

$$\mu_x^i(\rho) = \frac{\partial}{\partial \rho} \{ \rho \epsilon_x^i(\rho) \} = \epsilon_x^i(\rho) + \rho \frac{\partial \epsilon_x^i(\rho)}{\partial \rho} = \frac{4}{3} \epsilon_x^i(\rho) \quad \text{for } i = P, F \quad , \quad (10.1.30)$$

which, when combined with equation (10.1.19), results in the following expression for the exchange potential

$$\begin{aligned} v_{x,\sigma}(\rho, \zeta) &= \frac{4}{3} \epsilon_x^P(\rho) + \gamma [\epsilon_x^F(\rho) - \epsilon_x^P(\rho)] \left((1 + z_\sigma \zeta)^{\frac{1}{3}} - 1 \right) \\ &= \frac{4}{3} \epsilon_x^P(\rho) (1 + z_\sigma \zeta)^{\frac{1}{3}} \\ &= \frac{4}{3} \epsilon_x^P(\rho) \left(\frac{2\rho_\sigma}{\rho} \right)^{\frac{1}{3}} \quad , \\ &= \mu_x^P(\rho) \left(\frac{2\rho_\sigma}{\rho} \right)^{\frac{1}{3}} \\ &= \mu_x^P(2\rho_\sigma) \quad . \end{aligned} \quad (10.1.31)$$

Here we have used the RPA scaling (10.1.10), equation (10.1.26) as well as the identities (10.1.4) and (10.1.18). We have furthermore in the last line expressed the spin dependent exchange potential in terms of the paramagnetic potential in close analogy to equation (10.1.28). Of course, the same results is obtained from combining equations (10.1.7), (10.1.28), and (10.1.30),

$$\begin{aligned} v_{x,\sigma}(\rho_\uparrow, \rho_\downarrow) &= \left[\frac{\partial}{\partial \rho_\sigma} \{ \rho \epsilon_x(\rho_\uparrow, \rho_\downarrow) \} \right]_{\rho_\sigma = \rho_\sigma(\mathbf{r})} \\ &= \left[\frac{\partial}{\partial \rho} \{ \rho \epsilon_x^P(\rho) \} \right]_{\rho = 2\rho_\sigma(\mathbf{r})} \\ &= \mu_x^P(2\rho_\sigma) \quad . \end{aligned} \quad (10.1.32)$$

The previous expressions for the exchange energy density and potential as given by Kohn, Sham and Gaspár are common to all the density functionals described below, which, hence, deviate only with respect to their modelling of the correlation energy density. Before entering a more detailed discussion

of the latter we note, however, that in all schemes the contributions due to exchange and correlation add to each other,

$$\begin{aligned}\epsilon_{xc}(\rho, \zeta) &= \epsilon_x(\rho, \zeta) + \epsilon_c(\rho, \zeta) \\ &= \frac{1}{2}\epsilon_x^P(\rho) \left[\left(\frac{2\rho_\uparrow}{\rho}\right)^{\frac{4}{3}} + \left(\frac{2\rho_\downarrow}{\rho}\right)^{\frac{4}{3}} \right] \\ &\quad + \epsilon_c^P(\rho) + [\epsilon_c^F(\rho) - \epsilon_c^P(\rho)] f(\zeta) \quad . \quad (10.1.33)\end{aligned}$$

Here we used the spin interpolation formula (10.1.11) as well as the RPA scaling as inherent in equations (10.1.10) and (10.1.25). Contributions from exchange and correlation add up also in the non-spin-polarized and fully spin-polarized potential as given by equation (10.1.16) as well as in the spin-interpolated potential and, using equations (10.1.4), (10.1.19) and (10.1.31), we obtain the result

$$\begin{aligned}v_{xc,\sigma}(\rho, \zeta) &= v_{x,\sigma}(\rho, \zeta) + v_{c,\sigma}(\rho, \zeta) \\ &= \frac{4}{3}\epsilon_x^P(\rho) \left(\frac{2\rho_\sigma}{\rho}\right)^{\frac{4}{3}} + \mu_c^P(\rho) + [\mu_c^F(\rho) - \mu_c^P(\rho)] f(\zeta) \\ &\quad + [\epsilon_c^F(\rho) - \epsilon_c^P(\rho)] \left[\gamma \left((1 + z_\sigma \zeta)^{\frac{1}{3}} - 1 \right) - \frac{4}{3} f(\zeta) \right] \\ &= \left[\frac{4}{3}\epsilon_x^P(\rho) + \gamma (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \right] \left(\frac{2\rho_\sigma}{\rho}\right)^{\frac{4}{3}} \\ &\quad + \mu_c^P(\rho) - \gamma (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \\ &\quad + \left[\mu_c^F(\rho) - \mu_c^P(\rho) - \frac{4}{3} (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \right] f(\zeta) \\ &= \left[\frac{4}{3}\epsilon_x^P(\rho) + \nu_c(\rho) \right] \left(\frac{2\rho_\sigma}{\rho}\right)^{\frac{4}{3}} + \mu_c^P(\rho) - \nu_c(\rho) + \tau_c(\rho) f(\zeta) \quad , \quad (10.1.34)\end{aligned}$$

where in the last step we have abbreviated

$$\nu_c(\rho) = \gamma (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \quad , \quad (10.1.35)$$

$$\tau_c(\rho) = \mu_c^F(\rho) - \mu_c^P(\rho) - \frac{4}{3} (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \quad . \quad (10.1.36)$$

In this context it should again be noted that for the paramagnetic and the saturated ferromagnetic ground state the correlation potential trivially reduces to $\mu_c^P(r_S)$ and $\mu_c^F(r_S)$, respectively.

One of the most used parametrizations of the correlation energy density was first suggested by Hedin and Lundqvist (HL) [75], who, however, did not deal with the spin-polarized ground state. This was made up for later on by von Barth and Hedin (vBH) [17], who proposed to use the ρ -dependence of $\epsilon_c^P(\rho)$

as given by Hedin and Lundqvist also for $\epsilon_c^F(\rho)$. To be specific, von Barth and Hedin modelled the correlation energy density by

$$\epsilon_c^i(\rho) = -c_i \mathcal{G}\left(\frac{r_S}{r_i}\right) \quad \text{for } i = P, F \quad , \quad (10.1.37)$$

where

$$\mathcal{G}(x) = (1 + x^3) \ln\left(1 + \frac{1}{x}\right) + \frac{x}{2} - x^2 - \frac{1}{3} \quad . \quad (10.1.38)$$

In order to derive the correlation potential we first note

$$\mu_c^i = \frac{\partial}{\partial \rho} \{\rho \epsilon_c^i\} = \epsilon_c^i(\rho) + \rho \frac{\partial x}{\partial \rho} \frac{\partial \epsilon_c^i}{\partial x} \quad \text{for } i = P, F \quad , \quad (10.1.39)$$

where

$$x = \frac{r_S}{r_i} = \frac{1}{r_i} \left(\frac{3}{4\pi\rho}\right)^{\frac{1}{3}} \quad , \quad \rho \frac{\partial x}{\partial \rho} = -\frac{1}{3}x \quad . \quad (10.1.40)$$

Taking the derivative of \mathcal{G} with respect to x ,

$$\frac{d\mathcal{G}(x)}{dx} = 3x^2 \ln\left(1 + \frac{1}{x}\right) - \frac{1+x^3}{x+x^2} + \frac{1}{2} - 2x \quad , \quad (10.1.41)$$

we obtain

$$\begin{aligned} \mu_c^i(\rho) &= -c_i \mathcal{G}(x) + \frac{1}{3} c_i x \frac{d\mathcal{G}(x)}{dx} \\ &= -c_i \ln\left(1 + \frac{1}{x}\right) \\ &= -c_i \ln\left(1 + \frac{r_i}{r_S}\right) \quad \text{for } i = P, F \quad , \end{aligned} \quad (10.1.42)$$

Still, the scheme suggested by Hedin and Lundqvist as well as von Barth and Hedin depends on the four parameters r_P , r_F , c_P , and c_F . Different values for these parameters have been proposed, which are listed in Table 10.1. The

Scheme	r_P	r_F	c_P	c_F
HL / MJW	21.0	52.91668	0.045	0.0225
HL / JMW	21.0	26.4583	0.045	0.0357
vBH	30.0	75.0	0.0504	0.0254
GLW	11.4	15.9	0.0666	0.0406

Table 10.1: Parameters for the Hedin-Lundqvist parametrization of the correlation energy density.

first two lines give the parameters for the non-spin-polarized case as proposed by Hedin and Lundqvist as well as the parameters r_F and c_F as arising from different scalings of r_P and c_P . While Moruzzi, Janak and Williams (MJW) [117] used the exact RPA scaling,

$$r_F = 2^{\frac{4}{3}} r_P \quad , \quad c_F = \frac{1}{2} c_P \quad , \quad (10.1.43)$$

the parameter set proposed by von Barth and Hedin obeys this scaling approximately within an accuracy of 1%.

Another set was given by Gunnarsson, Lundqvist and Wilkins (GLW) [67], who, while still using the spin interpolation formula (10.1.11) for the exchange-correlation energy, proposed a different spin interpolation for the exchange-correlation potential,

$$v_{xc,\sigma}(\rho, \zeta) = \frac{4}{3} \epsilon_x^P(\rho) + \mu_c^P(\rho) - \frac{4}{9} \epsilon_0 \frac{\bar{\delta}(\rho)}{r_S} \frac{z_\sigma \zeta}{1 + \bar{\gamma} z_\sigma \zeta} \quad , \quad (10.1.44)$$

where

$$\bar{\delta}(\rho) = 1 - 0.036 r_S - \frac{1.36 r_S}{1 + 10 r_S} \quad , \quad (10.1.45)$$

and $\bar{\gamma} = 0.297$ [67] (Eq. (10.1.45) has been erroneously given with a plus sign in front of the last term in a later publication by Gunnarsson and Lundqvist [66]). Since we have from equation (10.1.3)

$$\zeta = \left(\frac{2\rho_\uparrow}{\rho} - 1 \right) = - \left(\frac{2\rho_\downarrow}{\rho} - 1 \right) \quad , \quad (10.1.46)$$

hence

$$z_\sigma \zeta = \left(\frac{2\rho_\sigma}{\rho} - 1 \right) \quad \text{for } \sigma = \uparrow, \downarrow \quad , \quad (10.1.47)$$

we arrive at the result

$$v_{xc,\sigma}(\rho, \zeta) = \frac{4}{3} \epsilon_x^P(\rho) + \mu_c^P(\rho) - \frac{4}{9} \epsilon_0 \frac{\bar{\delta}(\rho)}{r_S} \frac{\left(\frac{2\rho_\sigma}{\rho} - 1 \right)}{1 - \bar{\gamma} + \bar{\gamma} \frac{2\rho_\sigma}{\rho}} \quad . \quad (10.1.48)$$

Janak, Moruzzi and Williams (JMW) [83] later on adopted the same density and spin dependence of the energy density and potential as Gunnarsson, Lundqvist and Wilkins. They used, however, the parameters r_P and c_P as given by Hedin and Lundqvist and suggested to derive the parameters for the correlation energy density of the fully spin-polarized ground state from the scaling

$$r_F = 2^{\frac{1}{3}} r_P \quad , \quad c_F = 2^{-\frac{1}{3}} c_P \quad . \quad (10.1.49)$$

While all the previous schemes employed the same functional relationship for the energy density, albeit with different values for the parameters, the work

of Ceperley and Alder marked the starting point for new parametrizations [31, 30]. These authors performed Monte Carlo simulations for the homogeneous electron gas, which results later on gave rise to the parametrizations by Perdew and Zunger (PZ) [136] as well as by Vosko, Wilk and Nusair (VWN) [167]. However, as already mentioned these new parametrizations did not affect the exchange energy density and potential, which were incorporated as outlined above.

Perdew and Zunger [136] used a two-point Padé approximant to fit the correlation energy density to the Monte Carlo data by Ceperley and Alder. In doing so they furthermore distinguished the high and low density range and proposed the following form for the correlation energy density

$$\epsilon_c^i(\rho) = \begin{cases} \gamma_i (1 + \beta_1^i \sqrt{r_S} + \beta_2^i r_S)^{-1} & \text{for } r_S \geq 1 \\ A_i \ln r_S + B_i + C_i r_S \ln r_S + D_i r_S & \text{for } r_S < 1 \end{cases} \quad \text{for } i = P, F \quad . \quad (10.1.50)$$

The parameters given by Perdew and Zunger are listed in Table 10.2. Note that

i	γ_i	β_1^i	β_2^i	A_i	B_i	C_i	D_i
P	-0.2846	1.0529	0.3334	0.0622	-0.096	0.0040	-0.0232
F	-0.1686	1.3981	0.2611	0.0311	-0.0538	0.0014	-0.0096

Table 10.2: Parameters for the parametrization of the correlation energy density as given by Perdew and Zunger [136].

the values for γ_i , A_i , B_i , C_i , and D_i are twice as large as those originally listed by Perdew and Zunger, since these authors used Hartree atomic units instead of Rydberg atomic units. From equation (10.1.50) we obtain the following expressions for the correlation potential

$$\begin{aligned} \mu_c^i &= \epsilon_c^i(\rho) + \rho \frac{\partial r_S}{\partial \rho} \frac{\partial \epsilon_c^i}{\partial r_S} \\ &= \epsilon_c^i(\rho) - \frac{1}{3} r_S \frac{\partial \epsilon_c^i}{\partial r_S} \\ &= \begin{cases} \gamma_i (1 + \frac{7}{6} \beta_1^i \sqrt{r_S} + \frac{4}{3} \beta_2^i r_S) (1 + \beta_1^i \sqrt{r_S} + \beta_2^i r_S)^{-2} & \text{for } r_S \geq 1 \\ A_i \ln r_S + (B_i - \frac{1}{3} A_i) + \frac{2}{3} C_i r_S \ln r_S + \frac{1}{3} (2D_i - C_i) r_S & \text{for } r_S < 1 \end{cases} \\ &= \begin{cases} \frac{4(\epsilon_c^i)^2}{3\gamma_i} (\frac{3}{4} + \frac{7}{8} \beta_1^i \sqrt{r_S} + \beta_2^i r_S) & \text{for } r_S \geq 1 \\ \epsilon_c^i - \frac{1}{3} [A_i + (C_i(1 + \ln r_S) + D_i) r_S] & \text{for } r_S < 1 \end{cases} \\ &\quad \text{for } i = P, F \quad . \end{aligned} \quad (10.1.51)$$

Finally, in order to arrive at a full specification of the exchange-correlation energy density and potential, we have to feed the formulas (10.1.50) and (10.1.51) for the unpolarized and fully polarized correlation energy density and potential into the spin interpolation formulas (10.1.33) and (10.1.34).

Yet another parametrization of the Monte Carlo results by Ceperley and Alder was proposed by Vosko, Wilk and Nusair [167], who likewise performed a Padé approximation. This parametrization has the virtue of being continuous over r_S . Following Vosko *et al.*, Painter [122] and MacLaren *et al.* [107], we note

$$\begin{aligned}
\epsilon_c^i(\rho) &= A_i \left[\ln \frac{x^2}{X_i(x)} + \frac{2b_i}{Q_i} F_i(x) \right. \\
&\quad \left. - \frac{b_i x_{0,i}}{X_i(x_{0,i})} \left(\ln \frac{(x - x_{0,i})^2}{X_i(x)} + \frac{2(b_i + 2x_{0,i})}{Q_i} F_i(x) \right) \right] \\
&= A_i \left[\ln \frac{x^2}{X_i(x)} - \frac{b_i x_{0,i}}{X_i(x_{0,i})} \ln \frac{(x - x_{0,i})^2}{X_i(x)} \right. \\
&\quad \left. + \frac{2b_i}{Q_i X_i(x_{0,i})} \left(X_i(x_{0,i}) - x_{0,i}(b_i + 2x_{0,i}) \right) F_i(x) \right] \\
&\quad \text{for } i = P, F, S \quad , \quad (10.1.52)
\end{aligned}$$

where $x = \sqrt{r_S}$ and

$$X_i(x) = x^2 + b_i x + c_i, \quad Q_i = \sqrt{4c_i - b_i^2}, \quad F_i(x) = \arctan \frac{Q_i}{2x + b_i}, \quad (10.1.53)$$

and the parameters A_i , b_i , c_i , and $x_{0,i}$ are listed in Table 10.3. The parametriza-

i	A_i	b_i	c_i	$x_{0,i}$
P	$2(1 - \ln 2)/\pi^2 \approx 0.0621814$	3.72744	12.9352	-0.10498
F	$(1 - \ln 2)/\pi^2 \approx 0.0310907$	7.06042	18.0578	-0.32500
S	$-1/(3\pi^2) \approx -0.0337737$	1.13107	13.0045	-0.00475840

Table 10.3: Parameters for the parametrization of the correlation energy density and the spin stiffness as given by Vosko, Wilk and Nusair [167].

tion (10.1.52) is valid for the paramagnetic and the saturated ferromagnetic ground state. In addition, it holds for the spin stiffness (subscript S), which will be discussed below. For later use we note

$$\frac{dX_i(x)}{dx} = 2x + b_i, \quad \frac{dF_i(x)}{dx} = -\frac{Q_i}{2X_i(x)} \quad (10.1.54)$$

The correlation potential for the paramagnetic and saturated ferromagnetic ground state is then calculated along the lines of equation (10.1.16) as

$$\mu_c^i(\rho) = \epsilon_c^i(\rho) + \rho \frac{\partial}{\partial \rho} \epsilon_c^i(\rho)$$

$$= \epsilon_c^i(\rho) + \rho \frac{\partial r_S}{\partial \rho} \frac{\partial x}{\partial r_S} \frac{\partial \epsilon_c^i}{\partial x} = \epsilon_c^i(\rho) - \frac{x}{6} \frac{\partial \epsilon_c^i}{\partial x} \quad \text{for } i = P, F, S \quad , \quad (10.1.55)$$

where we have used equation (10.1.22). For the derivative of the energy density with respect to x we note the following detailed derivation

$$\begin{aligned} \frac{\partial \epsilon_c^i}{\partial x} &= A_i \left[\frac{X_i(x)}{x^2} \frac{2xX_i(x) - x^2(2x + b_i)}{X_i^2(x)} \right. \\ &\quad - \frac{b_i x_{0,i}}{X_i(x_{0,i})} \frac{X_i(x)}{(x - x_{0,i})^2} \frac{2(x - x_{0,i})X_i(x) - (x - x_{0,i})^2(2x + b_i)}{X_i^2(x)} \\ &\quad \left. - \frac{2b_i}{Q_i X_i(x_{0,i})} (X_i(x_{0,i}) - x_{0,i}(b_i + 2x_{0,i})) \frac{Q_i}{2X_i(x)} \right] \\ &= A_i \left[\frac{2}{x} - \left(1 - \frac{b_i x_{0,i}}{X_i(x_{0,i})} \right) \frac{2x + b_i}{X_i(x)} - \frac{2b_i x_{0,i}}{(x - x_{0,i})X_i(x_{0,i})} \right. \\ &\quad \left. - \left(1 - \frac{b_i + 2x_{0,i}}{X_i(x_{0,i})} x_{0,i} \right) \frac{b_i}{X_i(x)} \right] \\ &= A_i \left[\frac{2}{x} - \frac{2x + 2b_i}{X_i(x)} + b_i x_{0,i} \frac{2x + 2x_{0,i} + 2b_i}{X_i(x_{0,i})X_i(x)} - \frac{2b_i x_{0,i}}{(x - x_{0,i})X_i(x_{0,i})} \right] \\ &= 2A_i \left[\frac{c_i}{xX_i(x)} + b_i x_{0,i} \frac{(x + x_{0,i} + b_i)(x - x_{0,i}) - X_i(x)}{(x - x_{0,i})X_i(x_{0,i})X_i(x)} \right] \\ &= 2A_i \left[\frac{c_i}{xX_i(x)} - \frac{b_i x_{0,i}}{(x - x_{0,i})X_i(x)} \right] \\ &= 2A_i \left[\frac{c_i(x - x_{0,i}) - b_i x_{0,i} x}{x(x - x_{0,i})X_i(x)} \right] \\ &= \frac{2A_i}{x} \frac{c_i x_{0,i} + (b_i x_{0,i} - c_i)x}{c_i x_{0,i} + (b_i x_{0,i} - c_i)x + (x_{0,i} - b_i)x^2 - x^3} \\ &= \frac{2A_i}{x} \frac{1 + b_{1,i}x}{1 + b_{1,i}x + b_{2,i}x^2 + b_{3,i}x^3} \quad \text{for } i = P, F, S \quad , \quad (10.1.56) \end{aligned}$$

where

$$b_{1,i} = \frac{b_i x_{0,i} - c_i}{c_i x_{0,i}} \quad , \quad b_{2,i} = \frac{x_{0,i} - b_i}{c_i x_{0,i}} \quad , \quad b_{3,i} = -\frac{1}{c_i x_{0,i}} \quad . \quad (10.1.57)$$

Combining equations (10.1.55) and (10.1.56) we thus write down the result

$$\mu_c^i(\rho) = \epsilon_c^i(\rho) - \frac{A_i}{3} \frac{1 + b_{1,i}x}{1 + b_{1,i}x + b_{2,i}x^2 + b_{3,i}x^3} \quad \text{for } i = P, F, S \quad , \quad (10.1.58)$$

which, taken together with the spin interpolation formula (10.1.34), provides a full specification of the correlation potential.

However, in addition to the previous parametrization for the non-spin-polarized and the fully spin-polarized ground state, Vosko, Wilk and Nusair proposed a new spin interpolation formula for the correlation energy density, which they found superior to the formula (10.1.14) given by von Barth and Hedin. While still using this spin interpolation for the exchange energy, Vosko *et al.* wrote for the correlation energy density

$$\epsilon_c(\rho, \zeta) = \epsilon_c^P(\rho) + \Delta\epsilon_c(\rho, \zeta) \quad , \quad (10.1.59)$$

where

$$\Delta\epsilon_c(\rho, \zeta) = \epsilon_c^S(\rho) \frac{f(\zeta)}{f''(0)} [1 + \beta(\rho)\zeta^4] \quad . \quad (10.1.60)$$

Here, $\epsilon_c^S(\rho)$ is the spin stiffness, for which Vosko *et al.* gave the same parametrization (10.1.52) as for the non-spin-polarized and fully polarized correlation energy density. However, while Vosko *et al.* used the symbol $\alpha_c(\rho)$ for the spin stiffness we here prefer $\epsilon_c^S(\rho)$ for consistency in writing. The parameters for the spin stiffness are likewise included in Table 10.3.

The function $\beta(\rho)$ is evaluated from the condition that the correlation energy density $\epsilon_c(\rho, \zeta)$ matches $\epsilon_c^F(\rho)$ in the saturated ferromagnetic ground state, hence

$$\Delta\epsilon_c(\rho, 1) = \epsilon_c^F(\rho) - \epsilon_c^P(\rho) = \epsilon_c^S(\rho) \frac{1}{f''(0)} [1 + \beta(\rho)] \quad , \quad (10.1.61)$$

as

$$\beta(\rho) = f''(0) \frac{\epsilon_c^F(\rho) - \epsilon_c^P(\rho)}{\epsilon_c^S(\rho)} - 1 \quad . \quad (10.1.62)$$

Finally combining equations (10.1.59), (10.1.60), and (10.1.62) and inserting the identity $f''(0) = \gamma/3$ we arrive at a complete prescription of the correlation energy density as

$$\begin{aligned} \epsilon_c(\rho, \zeta) &= \epsilon_c^P(\rho) + \frac{3}{\gamma} \epsilon_c^S(\rho) f(\zeta) + \left[\epsilon_c^F(\rho) - \epsilon_c^P(\rho) - \frac{3}{\gamma} \epsilon_c^S(\rho) \right] \zeta^4 f(\zeta) \\ &= \epsilon_c^P(\rho) + \frac{3}{\gamma} \epsilon_c^S(\rho) (1 - \zeta^4) f(\zeta) + [\epsilon_c^F(\rho) - \epsilon_c^P(\rho)] \zeta^4 f(\zeta) \quad , \end{aligned} \quad (10.1.63)$$

which replaces the spin interpolation formula (10.1.33) given by von Barth and Hedin. In order to derive the corresponding formula for the correlation potential we go back to equation (10.1.9). Combining it with the identities (10.1.16) and (10.1.17) we obtain

$$v_{c,\sigma}(\rho, \zeta) = \mu_c^P(\rho) + \frac{3}{\gamma} \mu_c^S(\rho) (1 - \zeta^4) f(\zeta) + [\mu_c^F(\rho) - \mu_c^P(\rho)] \zeta^4 f(\zeta)$$

$$\begin{aligned}
& + \left[\frac{3}{\gamma} \epsilon_c^S(\rho) (1 - \zeta^4) + [\epsilon_c^F(\rho) - \epsilon_c^P(\rho)] \zeta^4 \right] \\
& \quad \left[\gamma \left((1 + z_\sigma \zeta)^{\frac{1}{3}} - 1 \right) - \frac{4}{3} f(\zeta) \right] \\
& + \left[\epsilon_c^F(\rho) - \epsilon_c^P(\rho) - \frac{3}{\gamma} \epsilon_c^S(\rho) \right] (z_\sigma - \zeta) 4 \zeta^3 f(\zeta) \\
= & \gamma (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \zeta^4 \left(\frac{2\rho_\sigma}{\rho} \right)^{\frac{1}{3}} + 3\epsilon_c^S(\rho) (1 - \zeta^4) \left(\frac{2\rho_\sigma}{\rho} \right)^{\frac{1}{3}} \\
& + \mu_c^P(\rho) - \gamma (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \zeta^4 - 3\epsilon_c^S(\rho) (1 - \zeta^4) \\
& + \left[\mu_c^F(\rho) - \mu_c^P(\rho) - \frac{4}{3} (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \right] \zeta^4 f(\zeta) \\
& + \frac{3}{\gamma} \left[\mu_c^S(\rho) - \frac{4}{3} \epsilon_c^S(\rho) \right] (1 - \zeta^4) f(\zeta) \\
& + 4 \left[\epsilon_c^F(\rho) - \epsilon_c^P(\rho) - \frac{3}{\gamma} \epsilon_c^S(\rho) \right] z_\sigma \zeta^3 (1 - z_\sigma \zeta) f(\zeta) \quad (10.1.64)
\end{aligned}$$

Using the identity (10.1.47) as well as the abbreviations (10.1.35) and (10.1.36), we arrive at the following final result for the exchange-correlation potential

$$\begin{aligned}
v_{xc,\sigma}(\rho, \zeta) & = \left[\frac{4}{3} \epsilon_x^P(\rho) + \gamma (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \zeta^4 + 3\epsilon_c^S(\rho) (1 - \zeta^4) \right] \left(\frac{2\rho_\sigma}{\rho} \right)^{\frac{1}{3}} \\
& + \mu_c^P(\rho) - \gamma (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \zeta^4 - 3\epsilon_c^S(\rho) (1 - \zeta^4) \\
& + \left[\mu_c^F(\rho) - \mu_c^P(\rho) - \frac{4}{3} (\epsilon_c^F(\rho) - \epsilon_c^P(\rho)) \right] \zeta^4 f(\zeta) \\
& + \frac{3}{\gamma} \left[\mu_c^S(\rho) - \frac{4}{3} \epsilon_c^S(\rho) \right] (1 - \zeta^4) f(\zeta) \\
& + 4 \left[\epsilon_c^F(\rho) - \epsilon_c^P(\rho) - \frac{3}{\gamma} \epsilon_c^S(\rho) \right] \left(2 - \frac{2\rho_\sigma}{\rho} \right) \left(\frac{2\rho_\sigma}{\rho} - 1 \right)^3 f(\zeta) \\
= & \left[\frac{4}{3} \epsilon_x^P(\rho) + \nu_c(\rho) \zeta^4 + 3\epsilon_c^S(\rho) (1 - \zeta^4) \right] \left(\frac{2\rho_\sigma}{\rho} \right)^{\frac{1}{3}} \\
& + \mu_c^P(\rho) - \lambda_c(\rho) \\
& + \tau_c(\rho) \zeta^4 f(\zeta) + \frac{3}{\gamma} \left[\mu_c^S(\rho) - \frac{4}{3} \epsilon_c^S(\rho) \right] (1 - \zeta^4) f(\zeta) \\
& + \frac{4}{\gamma} [\nu_c(\rho) - 3\epsilon_c^S(\rho)] \left(2 - \frac{2\rho_\sigma}{\rho} \right) \left(\frac{2\rho_\sigma}{\rho} - 1 \right)^3 f(\zeta) \quad , \\
& \hspace{15em} (10.1.65)
\end{aligned}$$

where in the last step we have defined

$$\lambda_c(\rho) = \nu_c(\rho) \zeta^4 + 3\epsilon_c^S(\rho) (1 - \zeta^4) \quad . \quad (10.1.66)$$

Equation (10.1.65) replaces the spin interpolation formula (10.1.34). Again we point out that the potential trivially reduces to $\mu_c^P(r_S)$ and $\mu_c^F(r_S)$ for $\zeta = 0$

and $\zeta = 1$, respectively.

Finally, a parametrization, which turned out to give similar results to that of Vosko, Wilk and Nusair, was presented by Perdew and Wang [135]. They proposed for the correlation energy density the relation

$$\epsilon_c^i(\rho) = -2A_i(1 + \alpha_i x^2) \ln\left(1 + \frac{1}{Q_i}\right) \quad \text{for } i = P, F, S \quad , \quad (10.1.67)$$

where $x = \sqrt{r_S}$ and

$$Q_i = 2A_i(\beta_1^i x + \beta_2^i x^2 + \beta_3^i x^3 + \beta_4^i x^4) \quad , \quad (10.1.68)$$

hence,

$$\frac{dQ_i}{dx} = 2A_i(\beta_1^i + 2\beta_2^i x + 3\beta_3^i x^2 + 4\beta_4^i x^3) =: Q_i' \quad . \quad (10.1.69)$$

The parameters arising from fitting the functional relationship (10.1.67) to the Monte Carlo data by Ceperley and Alder are listed in Table 10.4. Note that

i	A_i	α_i	β_1^i	β_2^i	β_3^i	β_4^i
P	$2(1 - \ln 2)/\pi^2$	0.21370	3.79785	1.79380	0.81910	0.24647
F	$(1 - \ln 2)/\pi^2$	0.20548	7.05945	3.09885	1.68310	0.312585
S	$-1/(3\pi^2)$	0.11125	-5.1785	-1.81155	-0.44013	-0.248355

Table 10.4: Parameters for the parametrization of the correlation energy density and the spin stiffness as given by Perdew and Wang [135].

the parameters A_i are identical to those given by Vosko, Wilk and Nusair (see Table 10.3) and that the values for A_i and β_j^i , $j = 1, \dots, 4$ are by a factor two larger and smaller, respectively than those originally listed by Perdew and Wang due to the use of Hartree atomic units by these authors. In order to calculate the correlation potential we derive from equation (10.1.67)

$$\frac{d\epsilon_c^i}{dx} = -4A_i\alpha_i x \ln\left(1 + \frac{1}{Q_i}\right) + 2A_i(1 + \alpha_i x^2) \frac{Q_i'}{Q_i + Q_i^2} \quad \text{for } i = P, F, S \quad , \quad (10.1.70)$$

and, inserting this into the identity (10.1.55), we obtain the result

$$\begin{aligned} \mu_c^i(\rho) &= \epsilon_c^i(\rho) + \frac{2}{3}A_i\alpha_i x^2 \ln\left(1 + \frac{1}{Q_i}\right) \\ &\quad - \frac{2}{3}A_i^2(1 + \alpha_i x^2) \frac{\beta_1^i x + 2\beta_2^i x^2 + 3\beta_3^i x^3 + 4\beta_4^i x^4}{Q_i + Q_i^2} \\ &\quad \text{for } i = P, F, S \quad , \quad (10.1.71) \end{aligned}$$

which, according to Perdew and Wang, like the correlation energy density above has to be combined with the spin interpolation formula given by Vosko, Wilk and Nusair [135] with the parameters given in Table 10.4 for the spin stiffness.

10.2 The adiabatic connection

Having described the local density approximation and given a number of parametrizations for its practical use, we might still like to look behind the scene and try to get deeper insight in the errors coming with it. In particular, we might still wonder why the local density approximation has proven to give excellent results in numerous cases. To enlighten this point a little, we turn to a different approach, which was thoroughly discussed by Harris and Jones [71], Gunnarsson and Lundqvist [66], Langreth and Perdew [99], as well as Harris [70] (the interested reader is also referred to an overview by Callaway and March [25]). These authors derived an exact expression for the exchange-correlation energy functional based on the pair-correlation function and proved that the local density approximation is just a special modelling of this function, which, however, fulfils an important sum rule.

In the course of the subsequent derivations we will make use of the Hellmann-Feynman theorem [77, 53], which is of a very general nature and applies to a vast number of situations (see also the book by Eschrig [42]). To be specific, we start out from a Hamiltonian, which is assumed to depend on a parameter λ . Of course, all eigenfunctions and eigenvalues will then also depend on this parameter and the eigenvalues are given by

$$\varepsilon_n(\lambda) = \frac{\langle \psi_n(\lambda) | H(\lambda) | \psi_n(\lambda) \rangle}{\langle \psi_n(\lambda) | \psi_n(\lambda) \rangle} . \quad (10.2.1)$$

Here n labels different eigenstates. According to the theorem by Hellmann and Feynman any eigenstate then fulfils the relation

$$\frac{\partial \varepsilon_n(\lambda)}{\partial \lambda} = \frac{\langle \psi_n(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \psi_n(\lambda) \rangle}{\langle \psi_n(\lambda) | \psi_n(\lambda) \rangle} . \quad (10.2.2)$$

The proof is easily performed. Using the abbreviation

$$N_n(\lambda) = \langle \psi_n(\lambda) | \psi_n(\lambda) \rangle \quad (10.2.3)$$

for the norm of each eigenfunction as well as Eq. (10.2.1) we write

$$\begin{aligned} & \frac{\partial \varepsilon_n(\lambda)}{\partial \lambda} \\ &= \left(\frac{\partial}{\partial \lambda} \frac{1}{N_n(\lambda)} \right) \langle \psi_n(\lambda) | H(\lambda) | \psi_n(\lambda) \rangle + \frac{1}{N_n(\lambda)} \left\langle \frac{\partial \psi_n(\lambda)}{\partial \lambda} | H(\lambda) | \psi_n(\lambda) \right\rangle \\ & \quad + \frac{1}{N_n(\lambda)} \langle \psi_n(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \psi_n(\lambda) \rangle + \frac{1}{N_n(\lambda)} \langle \psi_n(\lambda) | H(\lambda) | \frac{\partial \psi_n(\lambda)}{\partial \lambda} \rangle \\ &= \left(-\frac{1}{(N_n(\lambda))^2} \frac{\partial N_n(\lambda)}{\partial \lambda} \right) \varepsilon_n(\lambda) N_n(\lambda) \\ & \quad + \frac{1}{N_n(\lambda)} \langle \psi_n(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \psi_n(\lambda) \rangle + \varepsilon_n(\lambda) \frac{1}{N_n(\lambda)} \frac{\partial N_n(\lambda)}{\partial \lambda} \\ &= \frac{1}{N_n(\lambda)} \langle \psi_n(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \psi_n(\lambda) \rangle , \end{aligned} \quad (10.2.4)$$

which is just Eq. (10.2.2). In passing, we note the integrated Hellmann-Feynman theorem

$$\varepsilon_n(\lambda_2) - \varepsilon_n(\lambda_1) = \int_{\lambda_1}^{\lambda_2} d\lambda \frac{\langle \psi_n(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | \psi_n(\lambda) \rangle}{\langle \psi_n(\lambda) | \psi_n(\lambda) \rangle} , \quad (10.2.5)$$

which follows directly from Eq. (10.2.2).

After these preparations we turn to the aforementioned issue of obtaining more insight into the local density approximation. Actually, our discussion will even go further back to the basics of the Kohn-Sham equations. In Sec. 9.4 we established a close connection between an interacting electron system with density ρ and a corresponding interaction-free reference system with exactly the same density. The relationship between these two systems is at the center of the adiabatic connection. In order to be concrete, we aim at the identity (9.4.16), which proposes a different splitting of the functional $G[\rho]$ into the kinetic energy functional $T_s[\rho]$ and the exchange-correlation functional $E_{xc}[\rho]$. Combining Eq. (9.4.16) with Eq. (9.3.14) we write the exchange-correlation functional explicitly as

$$E_{xc}[\rho] = F_{LL}[\rho] - T_s[\rho] - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_\sigma(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} , \quad (10.2.6)$$

with the Levy-Lieb functional defined by Eq. (9.3.9), i.e.

$$F_{LL}[\rho] = \inf_{|\Psi\rangle \in S(\rho)} \langle \Psi | H_{el,kin}(\{\mathbf{r}_i\}) + H_{el-el}(\{\mathbf{r}_i\}) | \Psi \rangle . \quad (10.2.7)$$

In the adiabatic connection the latter definition is generalized to an arbitrary strength of the electron-electron interaction. We note

$$F_{LL,\lambda}[\rho] = \inf_{|\Psi\rangle \in S(\rho)} \langle \Psi | H_{el,kin}(\{\mathbf{r}_i\}) + \lambda H_{el-el}(\{\mathbf{r}_i\}) | \Psi \rangle , \quad (10.2.8)$$

where the electron-electron interaction is scaled by a factor λ . Of course, for $\lambda = 1$, the so generalized functional (10.2.8) reduces to the standard Levy-Lieb functional of the interacting electron system. In contrast, for $\lambda = 0$, we arrive at the non-interacting system and obtain

$$F_{LL,\lambda=0}[\rho] = T_s[\rho] . \quad (10.2.9)$$

To conclude, by varying the parameter λ we may continuously switch on the electron-electron interaction and thus make a connection between the fully interacting system and the non-interacting reference system introduced by Kohn and Sham. It is this explicit relationship, which makes the adiabatic connection an appealing approach to understanding the Kohn-Sham method as well as the local density approximation built on it.

With these notions at hand we are able to note for the exchange-correlation functional

$$\begin{aligned}
E_{xc}[\rho] &= F_{LL,\lambda=1}[\rho] - F_{LL,\lambda=0}[\rho] - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\
&= \int_0^1 d\lambda \frac{\partial F_{LL,\lambda}[\rho]}{\partial \lambda} - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\sigma}(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} ,
\end{aligned} \tag{10.2.10}$$

which is, except for the Hartree functional, i.e. the contribution arising from the classical Coulomb interaction, an integral of the derivative of the Levy-Lieb functional over the coupling strength.

In order to prepare for the following derivations we rewrite Eq. (10.2.8) as

$$F_{LL,\lambda}[\rho] = \langle \Psi_{\lambda}^{\rho} | H_{el,kin}(\{\mathbf{r}_i\}) + \lambda H_{el-el}(\{\mathbf{r}_i\}) | \Psi_{\lambda}^{\rho} \rangle , \tag{10.2.11}$$

where $|\Psi_{\lambda}^{\rho}\rangle$ is just that wave function, which, for each λ , minimizes the functional under the constraint to yield the correct density. The latter is, of course, the same for all values of λ . The constraint on the wave function can be explicitly formulated as

$$\rho(\mathbf{r}) = \langle \Psi_{\lambda}^{\rho} | \hat{\rho}(\mathbf{r}) | \Psi_{\lambda}^{\rho} \rangle = \langle \Psi_{\lambda}^{\rho} | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_{\lambda}^{\rho} \rangle . \tag{10.2.12}$$

Here we have used the definition (5.7.11) of the density operator. Calculating the Levy-Lieb functional for arbitrary λ then corresponds to minimizing the functional

$$\begin{aligned}
F_{LL,\lambda}[\rho] + \int d^3\mathbf{r} \left(v_{\lambda}(\mathbf{r}) - \frac{E_{\lambda}}{N} \right) \langle \Psi_{\lambda}^{\rho} | \hat{\rho}(\mathbf{r}) | \Psi_{\lambda}^{\rho} \rangle \\
= \langle \Psi_{\lambda}^{\rho} | H_{el,kin}(\{\mathbf{r}_i\}) + \lambda H_{el-el}(\{\mathbf{r}_i\}) + \sum_i v_{\lambda}(\mathbf{r}_i) - E_{\lambda} | \Psi_{\lambda}^{\rho} \rangle ,
\end{aligned} \tag{10.2.13}$$

where the position dependent Lagrange multiplier $v_{\lambda}(\mathbf{r}) - E_{\lambda}/N$ was introduced to ensure the constraint (5.7.12). The variation of Eq. (10.2.13) defines the eigenvalue problem of a Hamiltonian

$$H_{\lambda}(\{\mathbf{r}_i\}) = H_{el,kin}(\{\mathbf{r}_i\}) + \lambda H_{el-el}(\{\mathbf{r}_i\}) + \sum_i v_{\lambda}(\mathbf{r}_i) \tag{10.2.14}$$

with eigenvalues E_{λ} ,

$$\begin{aligned}
&H_{\lambda}(\{\mathbf{r}_i\}) | \Psi_{\lambda}^{\rho} \rangle \\
&= \left(H_{el,kin}(\{\mathbf{r}_i\}) + \lambda H_{el-el}(\{\mathbf{r}_i\}) + \sum_i v_{\lambda}(\mathbf{r}_i) \right) | \Psi_{\lambda}^{\rho} \rangle \\
&= E_{\lambda} | \Psi_{\lambda}^{\rho} \rangle .
\end{aligned} \tag{10.2.15}$$

At this point it is instructive to have a closer look at the Hamiltonian H_λ as given by Eq. (10.2.14). Obviously, the additional potential $\sum_i v_\lambda(\mathbf{r}_i)$, which we originally introduced as Lagrange parameter, is a multiplicative single-particle potential. It will be zero in case of $\lambda = 1$, when the full electron-electron interaction is “switched on”. In contrast, on reducing the electron-electron interaction this potential comes into play and eventually takes over the role of the electron-electron interaction. In other words, on decreasing λ we gradually replace the electron-electron interaction, a two-particle operator, by the single-particle potential. In doing so, we guarantee conservation of the local charge density.

According to the Hellmann-Feynman theorem the eigenvalues in Eq. (10.2.15) fulfil the identity

$$\begin{aligned} \frac{\partial E_\lambda}{\partial \lambda} &= \langle \Psi_\lambda^\rho | \frac{\partial H_\lambda}{\partial \lambda} | \Psi_\lambda^\rho \rangle \\ &= \langle \Psi_\lambda^\rho | H_{el-el}(\{\mathbf{r}_i\}) | \Psi_\lambda^\rho \rangle + \langle \Psi_\lambda^\rho | \frac{\partial}{\partial \lambda} \sum_i v_\lambda(\mathbf{r}_i) | \Psi_\lambda^\rho \rangle \\ &= \langle \Psi_\lambda^\rho | H_{el-el}(\{\mathbf{r}_i\}) | \Psi_\lambda^\rho \rangle + \int d^3 \mathbf{r} \rho(\mathbf{r}) \frac{\partial}{\partial \lambda} v_\lambda(\mathbf{r}) \quad . \end{aligned} \quad (10.2.16)$$

Comparing this to

$$\begin{aligned} E_\lambda &= \langle \Psi_\lambda^\rho | H_{el,kin}(\{\mathbf{r}_i\}) + \lambda H_{el-el}(\{\mathbf{r}_i\}) + \sum_i v_\lambda(\mathbf{r}_i) | \Psi_\lambda^\rho \rangle \\ &= F_{LL,\lambda}[\rho] + \langle \Psi_\lambda^\rho | \sum_i v_\lambda(\mathbf{r}_i) | \Psi_\lambda^\rho \rangle \quad , \end{aligned} \quad (10.2.17)$$

which follows directly from Eq. (10.2.15), we are able to note the intermediate result

$$\frac{\partial F_{LL,\lambda}[\rho]}{\partial \lambda} = \langle \Psi_\lambda^\rho | H_{el-el}(\{\mathbf{r}_i\}) | \Psi_\lambda^\rho \rangle \quad . \quad (10.2.18)$$

Finally, inserting this into Eq. (10.2.10) we obtain

$$\begin{aligned} E_{xc}[\rho] &= \int_0^1 d\lambda \langle \Psi_\lambda^\rho | H_{el-el}(\{\mathbf{r}_i\}) | \Psi_\lambda^\rho \rangle \\ &\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \frac{\rho_\sigma(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= \int_0^1 d\lambda \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \frac{P_{\sigma\sigma',\lambda}(\mathbf{r}; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \frac{\rho_\sigma(\mathbf{r})\rho_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &= - \int_0^1 d\lambda \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \frac{|\rho_{\sigma\sigma',\lambda}(\mathbf{r}; \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad , \end{aligned} \quad (10.2.19)$$

where we have used the expectation value of the Hamiltonian comprising the electron-electron interaction in the same manner as in Eq. (9.3.13). Finally, using the identities (5.7.31) and (5.7.33) for the pair-correlation function, we may still rewrite the result (10.2.19) as

$$\begin{aligned} E_{xc}[\rho] &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \int_0^1 d\lambda [g_{\sigma\sigma',\lambda}(\mathbf{r};\mathbf{r}') - 1] \\ &= \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} [\tilde{g}_{\sigma\sigma'}(\mathbf{r};\mathbf{r}') - 1] \quad , \quad (10.2.20) \end{aligned}$$

where in the last step we have used the definition

$$\tilde{g}_{\sigma\sigma'}(\mathbf{r};\mathbf{r}') = \int_0^1 d\lambda g_{\sigma\sigma',\lambda}(\mathbf{r};\mathbf{r}') \quad (10.2.21)$$

of the integrated pair-correlation function. Finally, defining the so-called exchange-correlation hole by

$$\rho_{xc,\sigma\sigma'}(\mathbf{r};\mathbf{r}') := \rho_{\sigma'}(\mathbf{r}') [\tilde{g}_{\sigma\sigma'}(\mathbf{r};\mathbf{r}') - 1] \quad , \quad (10.2.22)$$

we arrive at the important expression

$$E_{xc}[\rho] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho_{xc,\sigma\sigma'}(\mathbf{r};\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad , \quad (10.2.23)$$

which suggests to interpret the exchange-correlation functional as arising from the Coulomb interaction of the electron density with the exchange-correlation hole.

The foregoing considerations have several important consequences: First of all, we have by now established a one-to-one correspondence between the exchange-correlation energy functional and the pair-correlation functional or the exchange-correlation hole. For this reason, we may view any approximation to E_{xc} alternatively as an approximation to the pair-correlation function or to the exchange-correlation hole. Of course, this will allow for improved interpretation of approximations. We will come to this point below.

Second, from the definition of the function $P_{\sigma\sigma'}(\mathbf{r};\mathbf{r}')$, which, when integrated over both spatial coordinates and summed over both spins gives the probability of finding one particle somewhere and another particle somewhere else, hence, results in $N(N-1)$, we obtain the important sum rule

$$\sum_{\sigma'} \int d^3\mathbf{r}' \rho_{xc,\sigma\sigma'}(\mathbf{r};\mathbf{r}') = -1 \quad . \quad (10.2.24)$$

Finally, we observe that the exchange-correlation energy functional depends only on the spherical average of the exchange-correlation hole,

$$\rho_{xc,\sigma\sigma'}^{SA}(\mathbf{r};|\mathbf{r}-\mathbf{r}'|) = \frac{1}{4\pi} \int d\hat{\mathbf{r}} \rho_{xc,\sigma\sigma'}(\mathbf{r};\mathbf{r}') \quad (10.2.25)$$

via

$$E_{xc}[\rho] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \rho(\mathbf{r}) \int ds 4\pi s \rho_{xc,\sigma\sigma'}^{SA}(\mathbf{r}; s) \quad , \quad (10.2.26)$$

where we have set $s = |\mathbf{r} - \mathbf{r}'|$.

Using the previous expressions as well as the relationship between the exchange-correlation energy and the pair-correlation function we may now turn to approximations. Of course, our first choice is the local density approximation, which consists of replacing the exact function $\tilde{g}_{\sigma\sigma'}(\mathbf{r}; \mathbf{r}')$ by the corresponding expression for the homogeneous electron gas. To be specific, we note for the LDA

$$\rho_{xc,\sigma\sigma'}^{LDA}(\mathbf{r}; \mathbf{r}') := \rho_\sigma(\mathbf{r}) [\tilde{g}_{\sigma\sigma'}^{HEG}(\mathbf{r}; \mathbf{r}', \rho_\sigma(\mathbf{r}) - 1)] \quad , \quad (10.2.27)$$

$$\varepsilon_{xc}[\rho] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r}' \frac{\rho_{xc,\sigma\sigma'}^{LDA}(\mathbf{r}; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad , \quad (10.2.28)$$

and

$$E_{xc}[\rho] = \sum_{\sigma} \int d^3\mathbf{r} \rho_\sigma(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r}), \zeta(\mathbf{r})) \quad . \quad (10.2.29)$$

With these expressions as well as Eq. (7.4.7) we arrive at two important observations. First, the exchange-correlation hole of the LDA is spherical symmetric. Second, it does obey the sum rule (10.2.24).

10.3 Generalized gradient approximation

Despite the overwhelming success of the local density approximation, there have still been attempts to improve it. The earliest approach was made by Kohn and Sham themselves, who proposed to add a gradient correction term to the exchange-correlation energy density similar to the von Weizsäcker correction to the Thomas-Fermi theory. However, attempts along these lines were not convincing and in many cases the good agreement obtained from the local density approximation was even spoiled. In recent years, this gave rise to the development of more general schemes as e.g. the generalized gradient approximation (GGA), which has proven very successful in particular for the calculation of structural properties [134, 127, 133, 39, 130].

At the beginning of the discussion about gradient approximations we have to become aware of and, at the same time, release an important assumption underlying the parametrizations coming with the local density approximation outlined in the previous section, namely the spin symmetry of the exchange-correlation energy density. As mentioned in connection with the spin interpolation formula, equation (10.1.14), both the function $f(\zeta)$ and the energy density $\epsilon_{xc}(\rho, \zeta)$ were constructed to be symmetric in ζ and, hence, to retain their form under exchange of ρ_\uparrow and ρ_\downarrow . This became also obvious from equation

(10.1.27), where we have written the exchange energy density $\epsilon_x(\rho, \zeta)$ both in terms of the spin interpolation formula and as a sum of equal contributions from both spins. Note that the latter can not be done for most parametrizations of the correlation energy density. Yet, in the case of the exchange energy density the splitting into contributions from each spin is essential for the gradient correction to be discussed now. For this reason, we will from now on work with the second representation of the exchange energy density given in equation (10.1.27). As we have moreover discussed in connection with equations (10.1.28) and (10.1.29), the density weighted exchange energy density, $\rho\epsilon_x(\rho, \zeta)$ can be expressed in terms of the *paramagnetic* exchange energy density. Hence, we may concentrate on the spin-symmetric case first and only later generalize the results to the spin-polarized ground state.

Within the generalized gradient approximation the paramagnetic exchange energy density is written as

$$\epsilon_x^{P,GGA}(\rho, \xi) = \epsilon_x^{P,LDA}(\rho)F(\xi) \quad , \quad (10.3.1)$$

where

$$\xi = \frac{|\nabla\rho(\mathbf{r})|}{2k_F\rho(\mathbf{r})} = \frac{|\nabla\rho(\mathbf{r})|}{2(3\pi^2\rho(\mathbf{r}))^{1/3}\rho(\mathbf{r})} \quad (10.3.2)$$

is the scaled gradient of the electronic density and the function $F(\xi)$ comprises all the corrections due to the spatial variation of the electronic charge density. As for the local density approximation several parametrizations for this function have been proposed in the past. However, in order to keep our discussion of the generalized gradient approximation as simple as possible we postpone an explicit specification of the function $F(\xi)$. Defining, in addition to equation (10.3.2),

$$\xi_i = \frac{1}{2k_F\rho(\mathbf{r})} \frac{\partial\rho(\mathbf{r})}{\partial r_i} = \frac{1}{2(3\pi^2\rho(\mathbf{r}))^{1/3}\rho(\mathbf{r})} \frac{\partial\rho(\mathbf{r})}{\partial r_i} \quad (10.3.3)$$

we obtain

$$\xi = \left(\sum_i \xi_i^2 \right)^{\frac{1}{2}} \quad , \quad \text{hence,} \quad \frac{\partial\xi}{\partial\xi_i} = \frac{\xi_i}{\xi} \quad (10.3.4)$$

and are thus prepared to write the paramagnetic exchange potential as the variational derivative of the exchange energy,

$$\begin{aligned} \mu_x^{P,GGA}(\rho, \xi) &= \frac{\partial}{\partial\rho} \{ \rho\epsilon_x^{P,GGA}(\rho, \xi) \} + \frac{\partial\xi}{\partial\rho} \frac{\partial}{\partial\xi} \{ \rho\epsilon_x^{P,GGA}(\rho, \xi) \} \\ &\quad - \sum_i \frac{d}{dr_i} \frac{\partial}{\partial(2k_F\rho\xi_i)} \{ \rho\epsilon_x^{P,GGA}(\rho, \xi) \} \\ &= \epsilon_x^{P,GGA}(\rho, \xi) + \rho \frac{\partial\epsilon_x^{P,GGA}(\rho, \xi)}{\partial\rho} \\ &\quad - \frac{4}{3} \frac{\xi}{\rho} \frac{\partial}{\partial\xi} \{ \rho\epsilon_x^{P,GGA}(\rho, \xi) \} \end{aligned}$$

$$\begin{aligned}
& - \sum_i \frac{d}{dr_i} \frac{1}{2k_F \rho} \frac{\partial \xi}{\partial \xi_i} \rho \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \\
& = \epsilon_x^{P,GGA}(\rho, \xi) + \rho \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \rho} \\
& \quad - \frac{4}{3} \xi^2 \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} \\
& \quad - \sum_i \frac{d}{dr_i} \frac{1}{2k_F} \frac{\xi_i}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} . \tag{10.3.5}
\end{aligned}$$

Here we have used the identity

$$\frac{\partial \xi}{\partial \rho} = -\frac{4}{3} \frac{\xi}{\rho} , \tag{10.3.6}$$

which follows from equation (10.3.2). The total derivative with respect to r_i is expressed in terms of the partial derivatives,

$$\frac{d}{dr_i} = \frac{\partial \rho}{\partial r_i} \frac{\partial}{\partial \rho} + \sum_j \frac{\partial \xi_j}{\partial r_i} \frac{\partial}{\partial \xi_j} + \frac{\partial}{\partial r_i} , \tag{10.3.7}$$

for which we use in addition

$$\sum_j \frac{\partial \xi_j}{\partial r_i} \frac{\partial}{\partial \xi_j} = \sum_j \frac{\partial \xi_j}{\partial r_i} \frac{\partial \xi}{\partial \xi_j} \frac{\partial}{\partial \xi} = \sum_j \frac{\xi_j}{\xi} \frac{\partial \xi_j}{\partial r_i} \frac{\partial}{\partial \xi} = \frac{\partial \xi}{\partial r_i} \frac{\partial}{\partial \xi} . \tag{10.3.8}$$

Inserting this into equation (10.3.5) we write for the potential

$$\begin{aligned}
& \mu_x^{P,GGA}(\rho, \xi) \\
& = \epsilon_x^{P,GGA}(\rho, \xi) + \rho \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \rho} - \frac{4}{3} \xi^2 \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} \\
& \quad - \sum_i \left[2k_F \rho \xi_i \frac{\partial}{\partial \rho} + \frac{\partial \xi}{\partial r_i} \frac{\partial}{\partial \xi} + \frac{\partial}{\partial r_i} \right] \frac{1}{2k_F} \frac{\xi_i}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} . \tag{10.3.9}
\end{aligned}$$

The terms in square brackets can be further simplified. Using

$$\frac{\partial}{\partial \rho} \frac{1}{2k_F} = -\frac{1}{6} \frac{3\pi^2}{k_F^4} = -\frac{1}{6} \frac{1}{k_F \rho} \tag{10.3.10}$$

as well as the fact that, according to the definitions (10.3.2) and (10.3.3), the quotient ξ_i/ξ does not depend on ρ we first note

$$\begin{aligned}
& \sum_i 2k_F \rho \xi_i \frac{\partial}{\partial \rho} \frac{1}{2k_F} \frac{\xi_i}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \\
& = 2k_F \rho \xi \frac{\partial}{\partial \rho} \frac{1}{2k_F} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi}
\end{aligned}$$

$$\begin{aligned}
&= 2k_F\rho\xi \left[-\frac{1}{6} \frac{1}{k_F\rho} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} + \frac{1}{2k_F} \frac{\partial^2 \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \rho \partial \xi} \right. \\
&\quad \left. + \frac{1}{2k_F} \frac{\partial \xi}{\partial \rho} \frac{\partial^2 \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi^2} \right] \\
&= \xi \left[-\frac{1}{3} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} + \rho \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \rho \partial \xi} \right] \\
&\quad - \frac{4}{3} \xi^2 \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} - \frac{4}{3} \xi^3 \frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} , \tag{10.3.11}
\end{aligned}$$

where in the last step we have used equation (10.3.6) and the identity

$$\frac{\partial^2 \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi^2} = \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} + \xi \frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} . \tag{10.3.12}$$

For the second term in square brackets in equation (10.3.9) we use

$$\frac{\partial \xi}{\partial r_i} = \frac{\partial}{\partial r_i} \frac{|\nabla \rho|}{2k_F \rho} = \frac{1}{2k_F \rho} \frac{\partial |\nabla \rho|}{\partial r_i} . \tag{10.3.13}$$

Inserting the previous identities into equation (10.3.9) we thus arrive at the following result for the paramagnetic exchange potential

$$\begin{aligned}
&\mu_x^{P,GGA}(\rho, \xi) \\
&= \epsilon_x^{P,GGA}(\rho, \xi) + \rho \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \rho} \\
&\quad - \xi \left[-\frac{1}{3} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} + \rho \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \rho \partial \xi} \right] \\
&\quad - \sum_i \left[\frac{1}{(2k_F)^2 \rho} \frac{\partial |\nabla \rho|}{\partial r_i} \xi_i - \frac{4}{3} \xi^3 \right] \frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} \\
&\quad - \sum_i \frac{1}{2k_F} \frac{\partial \xi_i}{\partial r_i} \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} \\
&= \epsilon_x^{P,GGA}(\rho, \xi) + \rho \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \rho} \\
&\quad - \xi \left[-\frac{1}{3} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} + \rho \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \rho \partial \xi} \right] \\
&\quad - \left[\frac{1}{(2k_F)^3 \rho^2} \nabla |\nabla \rho| \cdot \nabla \rho - \frac{4}{3} \xi^3 \right] \frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} \\
&\quad - \frac{1}{(2k_F)^2 \rho} \nabla^2 \rho \left\{ \frac{1}{\xi} \frac{\partial \epsilon_x^{P,GGA}(\rho, \xi)}{\partial \xi} \right\} . \tag{10.3.14}
\end{aligned}$$

Next we combine this result with equation (10.3.1) and, using the identity (10.1.30), we obtain

$$\mu_x^{P,GGA}(\rho, \xi)$$

$$\begin{aligned}
&= \mu_x^{P,LDA}(\rho)F(\xi) - \xi \left[-\frac{1}{3}\epsilon_x^{P,LDA}(\rho) + \rho \frac{\partial \epsilon_x^{P,LDA}(\rho)}{\partial \rho} \right] \frac{\partial F(\xi)}{\partial \xi} \\
&\quad - \left[\frac{1}{(2k_F)^3 \rho^2} \nabla |\nabla \rho| \cdot \nabla \rho - \frac{4}{3} \xi^3 \right] \epsilon_x^{P,LDA}(\rho) \frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial F(\xi)}{\partial \xi} \right\} \\
&\quad - \frac{1}{(2k_F)^2 \rho} \nabla^2 \rho \epsilon_x^{P,LDA}(\rho) \left\{ \frac{1}{\xi} \frac{\partial F(\xi)}{\partial \xi} \right\} . \tag{10.3.15}
\end{aligned}$$

According to the definition (10.1.27) of the paramagnetic exchange energy density the first square bracket vanishes and we are thus left with the final result

$$\begin{aligned}
&\mu_x^{P,GGA}(\rho, \xi) \\
&= \epsilon_x^{P,LDA}(\rho) \left[\frac{4}{3} F(\xi) - \frac{1}{(2k_F)^2 \rho} \nabla^2 \rho \left\{ \frac{1}{\xi} \frac{\partial F(\xi)}{\partial \xi} \right\} \right. \\
&\quad \left. - \left(\frac{1}{(2k_F)^3 \rho^2} \nabla |\nabla \rho| \cdot \nabla \rho - \frac{4}{3} \xi^3 \right) \frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial F(\xi)}{\partial \xi} \right\} \right] \\
&= \mu_x^{P,LDA}(\rho) \left[F(\xi) - \frac{3}{4} \frac{1}{(2k_F)^2 \rho} \nabla^2 \rho \left\{ \frac{1}{\xi} \frac{\partial F(\xi)}{\partial \xi} \right\} \right. \\
&\quad \left. - \left(\frac{3}{4} \frac{1}{(2k_F)^3 \rho^2} \nabla |\nabla \rho| \cdot \nabla \rho - \xi^3 \right) \frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial F(\xi)}{\partial \xi} \right\} \right] , \tag{10.3.16}
\end{aligned}$$

which is identical to equation (24) of Ref. [134].

In order to derive expressions for the spin-polarized exchange energy density and potential we start out from equations (10.1.28) as well as (10.1.31) and combine them with equations (10.3.1) and (10.3.16). Hence we note

$$\begin{aligned}
&\rho \epsilon_x^{GGA}(\rho, \zeta, \xi) \\
&= \frac{1}{2} [2\rho_\uparrow \epsilon_x^{P,GGA}(2\rho_\uparrow, \xi_\uparrow) + 2\rho_\downarrow \epsilon_x^{P,GGA}(2\rho_\downarrow, \xi_\downarrow)] \\
&= \frac{1}{2} [2\rho_\uparrow \epsilon_x^{P,LDA}(2\rho_\uparrow)F(\xi_\uparrow) + 2\rho_\downarrow \epsilon_x^{P,LDA}(2\rho_\downarrow)F(\xi_\downarrow)] \\
&= \frac{1}{2} \rho \left[\epsilon_x^{P,LDA}(\rho) \left(\frac{2\rho_\uparrow}{\rho} \right)^{\frac{4}{3}} F(\xi_\uparrow) + \epsilon_x^{P,LDA}(\rho) \left(\frac{2\rho_\downarrow}{\rho} \right)^{\frac{4}{3}} F(\xi_\downarrow) \right] , \tag{10.3.17}
\end{aligned}$$

where we have used the definition

$$\xi_\sigma := \frac{|\nabla \rho_\sigma(\mathbf{r})|}{2k_{F\sigma} \rho_\sigma(\mathbf{r})} := \frac{|\nabla \rho_\sigma(\mathbf{r})|}{2(6\pi^2 \rho_\sigma(\mathbf{r}))^{1/3} \rho_\sigma(\mathbf{r})} . \tag{10.3.18}$$

We may thus finally complement equation (10.1.27) with its GGA counterpart

$$\epsilon_x^{GGA}(\rho, \zeta, \xi) = \frac{1}{2} \epsilon_x^{P,LDA}(\rho) \left[\left(\frac{2\rho_\uparrow}{\rho} \right)^{\frac{4}{3}} F(\xi_\uparrow) + \left(\frac{2\rho_\downarrow}{\rho} \right)^{\frac{4}{3}} F(\xi_\downarrow) \right] . \tag{10.3.19}$$

It is important to note that, since ξ_σ is not symmetric with respect to exchanging σ by $-\sigma$, we cannot rewrite equation (10.3.19) in a form analogous to the first line of equation (10.1.27).

For the potential we start out from equations (10.1.31) and (10.1.32) and combine them with the intermediate result (10.3.16). We thus arrive at the final result

$$\begin{aligned}
v_{x,\sigma}^{GGA}(\rho, \zeta, \xi) &= \mu_x^{P,GGA}(2\rho_\sigma, \xi_\sigma) \\
&= \mu_x^{P,LDA}(2\rho_\sigma) \left[F(\xi_\sigma) - \frac{3}{4} \frac{1}{(2k_{F\sigma})^2 \rho_\sigma} \nabla^2 \rho_\sigma \left\{ \frac{1}{\xi_\sigma} \frac{\partial F(\xi_\sigma)}{\partial \xi_\sigma} \right\} \right. \\
&\quad \left. - \left(\frac{3}{4} \frac{1}{(2k_{F\sigma})^3 \rho_\sigma^2} \nabla |\nabla \rho_\sigma| \cdot \nabla \rho_\sigma - \xi_\sigma^3 \right) \frac{\partial}{\partial \xi_\sigma} \left\{ \frac{1}{\xi_\sigma} \frac{\partial F(\xi_\sigma)}{\partial \xi_\sigma} \right\} \right] \\
&= v_{x,\sigma}^{LDA}(\rho, \zeta) \left[F(\xi_\sigma) - \frac{3}{4} \frac{1}{(2k_{F\sigma})^2 \rho_\sigma} \nabla^2 \rho_\sigma \left\{ \frac{1}{\xi_\sigma} \frac{\partial F(\xi_\sigma)}{\partial \xi_\sigma} \right\} \right. \\
&\quad \left. - \left(\frac{3}{4} \frac{1}{(2k_{F\sigma})^3 \rho_\sigma^2} \nabla |\nabla \rho_\sigma| \cdot \nabla \rho_\sigma - \xi_\sigma^3 \right) \frac{\partial}{\partial \xi_\sigma} \left\{ \frac{1}{\xi_\sigma} \frac{\partial F(\xi_\sigma)}{\partial \xi_\sigma} \right\} \right] .
\end{aligned} \tag{10.3.20}$$

Note that $2\rho_\sigma$ appears only in the spin dependent scaled gradient, ξ_σ , via the spin dependent Fermi wave vector, $k_{F\sigma} = (6\pi^2 \rho_\sigma(\mathbf{r}))^{1/3}$, while the factor 2 cancels out in all other places.

As already mentioned above several parametrizations for the function $F(\xi)$ have been given in the literature. The first one goes back to Perdew and Wang (PW86) [134], who fitted numerical results and proposed

$$F(\xi) = (1 + a\xi^2/m + b\xi^4 + c\xi^6)^m \quad , \tag{10.3.21}$$

where $m = 1/15$, $a = 0.0864$, $b = 14$, and $c = 0.2$. Lateron, Perdew and Wang (PW91) [128, 129, 133] presented a refined approach,

$$F(\xi) = \frac{1 + a_1 \xi \sinh^{-1}(a_2 \xi) + (a_3 - a_4 e^{-m\xi^2}) \xi^2}{1 + a_1 \xi \sinh^{-1}(a_2 \xi) + a_5 \xi^4} \quad , \tag{10.3.22}$$

with the parameters listed in Table 10.5. These parametrizations are also referred to as PW GGA-I and PW GGA-II, respectively.

Yet another parametrization was given by Engel and Vosko (EV93) [39], who aimed, in particular, at improving the exchange potential rather than the energy. Using a [3/3]-Padé approximation to numerical data obtained from exact exchange calculations for spherical atoms these authors proposed

$$F(\xi) = \frac{1 + a_1 \xi^2 + a_2 \xi^4 + a_3 \xi^6}{1 + b_1 \xi^2 + b_2 \xi^4 + b_3 \xi^6} \tag{10.3.23}$$

a_1	a_2	a_3	a_4	m	a_5
0.19645	7.7956	0.2743	0.1508	100	0.004

Table 10.5: Parameters for the Perdew-Wang 1991 parametrization of the generalized gradient approximation to the exchange energy density.

a_1	a_2	a_3	b_1	b_2	b_3
1.647127	0.980118	0.017399	1.523671	0.367229	0.011282

Table 10.6: Parameters for the Engel-Vosko parametrization of the generalized gradient approximation to the exchange energy density.

with the coefficients listed in Table 10.6. More recently, Perdew, Burke and Ernzerhof (PBE96) [130, 132] presented a rather simple parametrization,

$$F(\xi) = 1 + \kappa - \frac{\kappa}{1 + \mu \xi^2 / \kappa} \quad , \quad (10.3.24)$$

where $\kappa = 0.804$ and $\mu = 0.21951$. The derivatives of the function $F(\xi)$ necessary to calculate the exchange potential (10.3.16) with the previous parametrizations are given in the Appendix A.1.

Within the generalized gradient approximation the correlation energy density still retains its spin-symmetric form as in the local density approximation. Following the work by Perdew *et al.* [133] we write

$$\epsilon_c^{GGA}(\rho, \zeta, \bar{\xi}) = \epsilon_c^{LDA}(\rho, \zeta) + H(\rho, \zeta, \bar{\xi}) \quad , \quad (10.3.25)$$

where ζ is the spin polarization as given by equation (10.1.3) and $\bar{\xi}$ is another scaled gradient of the density,

$$\bar{\xi} = \frac{|\nabla \rho(\mathbf{r})|}{2g(\zeta)k_S\rho(\mathbf{r})} \quad , \quad (10.3.26)$$

with the spin interpolation function

$$g(\zeta) = \frac{1}{2} \left[\left(\frac{2\rho_{\uparrow}}{\rho} \right)^{\frac{2}{3}} + \left(\frac{2\rho_{\downarrow}}{\rho} \right)^{\frac{2}{3}} \right] = \frac{1}{2} \left[(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3} \right] \quad (10.3.27)$$

which is displayed in Fig. 10.2, and the local screening vector

$$k_S = \left(\frac{4k_F}{\pi} \right)^{1/2} = \left(\frac{4(3\pi^2\rho(\mathbf{r}))^{1/3}}{\pi} \right)^{1/2} \quad . \quad (10.3.28)$$

In analogy to equation (10.3.3) we define in addition to equation (10.3.26)

$$\bar{\xi}_i = \frac{1}{2g(\zeta)k_S\rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial r_i} = \frac{\sqrt{\pi}}{4(3\pi^2\rho(\mathbf{r}))^{1/6}\rho(\mathbf{r})} \frac{\partial \rho(\mathbf{r})}{\partial r_i} \quad (10.3.29)$$

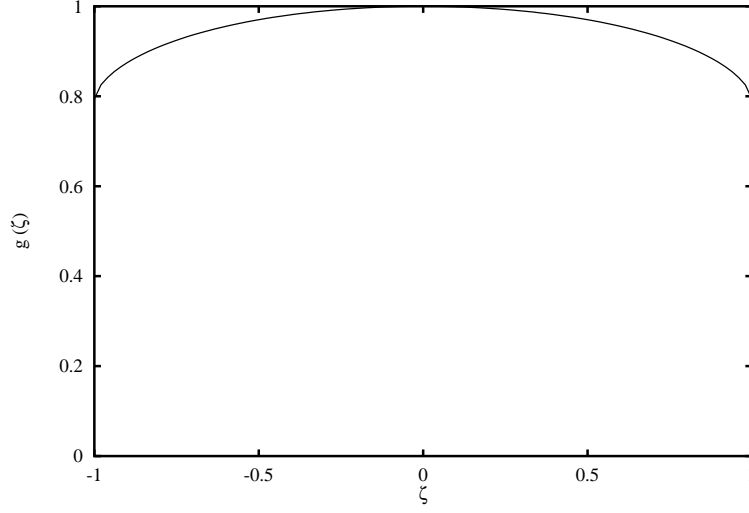


Figure 10.2: Spin polarization interpolation function $g(\zeta)$ as given by equation (10.3.27).

and obtain

$$\bar{\xi} = \left(\sum_i \bar{\xi}_i^2 \right)^{\frac{1}{2}}, \quad \text{hence,} \quad \frac{\partial \bar{\xi}}{\partial \bar{\xi}_i} = \frac{\bar{\xi}_i}{\bar{\xi}}, \quad (10.3.30)$$

which is formally identical to equation (10.3.4).

In the same way as for the exchange potential above the correlation potential arises as the variational derivative of the correlation energy density,

$$\begin{aligned} v_{c,\sigma}^{GGA}(\rho, \zeta, \bar{\xi}) &= \frac{\partial}{\partial \rho_\sigma} \{ \rho \epsilon_c^{GGA}(\rho, \zeta, \bar{\xi}) \} - \sum_i \frac{d}{dr_i} \frac{\partial}{\partial (2g(\zeta)k_S \rho \bar{\xi}_i)} \{ \rho \epsilon_c^{GGA}(\rho, \zeta, \bar{\xi}) \} \\ &= \frac{\partial}{\partial \rho_\sigma} \{ \rho \epsilon_c^{GGA}(\rho, \zeta, \bar{\xi}) \} - \sum_i \frac{d}{dr_i} \frac{1}{2g(\zeta)k_S \rho} \frac{\partial \bar{\xi}}{\partial \bar{\xi}_i} \rho \frac{\partial \epsilon_c^{GGA}(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \\ &= \frac{\partial}{\partial \rho_\sigma} \{ \rho \epsilon_c^{GGA}(\rho, \zeta, \bar{\xi}) \} - \sum_i \frac{d}{dr_i} \frac{1}{2g(\zeta)k_S} \frac{\bar{\xi}_i}{\bar{\xi}} \frac{\partial \epsilon_c^{GGA}(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \\ &= v_{c,\sigma}^{LDA}(\rho, \zeta) + \frac{\partial}{\partial \rho_\sigma} \{ \rho H(\rho, \zeta, \bar{\xi}) \} - \sum_i \frac{d}{dr_i} \frac{1}{2g(\zeta)k_S} \frac{\bar{\xi}_i}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} . \end{aligned} \quad (10.3.31)$$

The total derivative with respect to r_i is expressed in terms of the partial

derivatives as

$$\begin{aligned} \frac{d}{dr_i} &= \frac{\partial \rho}{\partial r_i} \frac{\partial}{\partial \rho} + \frac{\partial \zeta}{\partial r_i} \frac{\partial}{\partial \zeta} + \sum_j \frac{\partial \bar{\xi}_j}{\partial r_i} \frac{\partial}{\partial \bar{\xi}_j} + \frac{\partial}{\partial r_i} \\ &= \frac{\partial \rho}{\partial r_i} \frac{\partial}{\partial \rho} + \frac{\partial \zeta}{\partial r_i} \frac{\partial}{\partial \zeta} + \frac{\partial \bar{\xi}}{\partial r_i} \frac{\partial}{\partial \bar{\xi}} + \frac{\partial}{\partial r_i} \quad , \end{aligned} \quad (10.3.32)$$

where we have used the formal identity to equation (10.3.8). Combining this with equation (10.3.31) we obtain

$$\begin{aligned} v_{c,\sigma}^{GGA}(\rho, \zeta, \bar{\xi}) &= v_{c,\sigma}^{LDA}(\rho, \zeta) + \frac{\partial}{\partial \rho_\sigma} \{ \rho H(\rho, \zeta, \bar{\xi}) \} \\ &\quad - \sum_i \left[2g(\zeta) k_S \rho \bar{\xi}_i \frac{\partial}{\partial \rho} + \frac{\partial \zeta}{\partial r_i} \frac{\partial}{\partial \zeta} + \frac{\partial \bar{\xi}}{\partial r_i} \frac{\partial}{\partial \bar{\xi}} + \frac{\partial}{\partial r_i} \right] \\ &\quad \frac{1}{2g(\zeta) k_S} \frac{\bar{\xi}_i}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \quad . \end{aligned} \quad (10.3.33)$$

In order to simplify the terms in square brackets we derive from equation (10.3.28)

$$\frac{\partial}{\partial \rho} \frac{1}{2k_S} = \frac{\partial}{\partial \rho} \frac{\sqrt{\pi}}{4(3\pi^2\rho)^{1/6}} = -\frac{1}{6} \frac{1}{2k_S\rho} \quad (10.3.34)$$

and use the fact that according to the definitions (10.3.26) and (10.3.29) the quotient $\bar{\xi}_i/\bar{\xi}$ does depend neither on the density nor on the spin polarization. We thus note

$$\begin{aligned} &\sum_i 2g(\zeta) k_S \rho \bar{\xi}_i \frac{\partial}{\partial \rho} \frac{1}{2g(\zeta) k_S} \frac{\bar{\xi}_i}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \\ &= 2k_S \rho \bar{\xi} \frac{\partial}{\partial \rho} \frac{1}{2k_S} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \\ &= 2k_S \rho \bar{\xi} \left[-\frac{1}{6} \frac{1}{2k_S\rho} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} + \frac{1}{2k_S} \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \rho \partial \bar{\xi}} \right. \\ &\quad \left. + \frac{1}{2k_S} \frac{\partial \bar{\xi}}{\partial \rho} \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}^2} \right] \\ &= \bar{\xi} \left[-\frac{1}{6} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} + \rho \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \rho \partial \bar{\xi}} \right] \\ &\quad - \frac{7}{6} \bar{\xi}^2 \left\{ \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right\} - \frac{7}{6} \bar{\xi}^3 \frac{\partial}{\partial \bar{\xi}} \left\{ \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right\} \quad , \end{aligned} \quad (10.3.35)$$

where we have used the identity (10.3.12) for the second derivative of $H(\rho, \zeta, \bar{\xi})$ with respect to $\bar{\xi}$, and

$$\begin{aligned}
& \frac{\partial \zeta}{\partial r_i} \frac{\partial}{\partial \zeta} \frac{1}{2g(\zeta)k_S} \frac{\bar{\xi}_i}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \\
&= \frac{1}{2g(\zeta)k_S \rho} \frac{1}{\bar{\xi}} \nabla \rho \cdot \nabla \zeta \frac{\partial}{\partial \zeta} \frac{1}{2g(\zeta)k_S} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \\
&= \frac{1}{2g(\zeta)k_S \rho} \frac{1}{\bar{\xi}} \nabla \rho \cdot \nabla \zeta \left[\frac{1}{2g(\zeta)k_S} \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \zeta \partial \bar{\xi}} \right. \\
&\quad \left. + \frac{1}{2g(\zeta)k_S} \frac{\partial \bar{\xi}}{\partial \zeta} \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}^2} \right. \\
&\quad \left. - \frac{1}{2g(\zeta)k_S} \frac{g'(\zeta)}{g(\zeta)} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right] \\
&= \frac{1}{(2g(\zeta)k_S)^2 \rho} \nabla \rho \cdot \nabla \zeta \left[\frac{1}{\bar{\xi}} \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \zeta \partial \bar{\xi}} \right. \\
&\quad \left. - \frac{g'(\zeta)}{g(\zeta)} \left(\frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}^2} + \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right) \right] \\
&= \frac{1}{(2g(\zeta)k_S)^2 \rho} \nabla \rho \cdot \nabla \zeta \left[\frac{1}{\bar{\xi}} \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \zeta \partial \bar{\xi}} \right. \\
&\quad \left. - \frac{g'(\zeta)}{g(\zeta)} \left(\frac{2}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right) \right. \\
&\quad \left. + \bar{\xi} \frac{\partial}{\partial \bar{\xi}} \left\{ \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right\} \right] . \tag{10.3.36}
\end{aligned}$$

Here we have used the identity

$$\frac{\partial \bar{\xi}}{\partial \zeta} = -\frac{g'(\zeta)}{g(\zeta)} \bar{\xi} . \tag{10.3.37}$$

For the third term in square brackets in equation (10.3.33) we use

$$\frac{\partial \bar{\xi}}{\partial r_i} = \frac{\partial}{\partial r_i} \frac{|\nabla \rho|}{2g(\zeta)k_S \rho} = \frac{1}{2g(\zeta)k_S \rho} \frac{\partial |\nabla \rho|}{\partial r_i} . \tag{10.3.38}$$

Finally, we rewrite the derivative with respect to ρ_σ in close analogy to equation (10.1.8) as

$$\begin{aligned}
\frac{\partial}{\partial \rho_\sigma} &= \frac{\partial \rho}{\partial \rho_\sigma} \frac{\partial}{\partial \rho} + \frac{\partial \zeta}{\partial \rho_\sigma} \frac{\partial}{\partial \zeta} + \frac{\partial \bar{\xi}}{\partial \rho_\sigma} \frac{\partial}{\partial \bar{\xi}} \\
&= \frac{\partial}{\partial \rho} + \frac{z_\sigma - \zeta}{\rho} \frac{\partial}{\partial \zeta} + \left[\frac{\partial \rho}{\partial \rho_\sigma} \frac{\partial \bar{\xi}}{\partial \rho} + \frac{\partial \zeta}{\partial \rho_\sigma} \frac{\partial \bar{\xi}}{\partial \zeta} \right] \frac{\partial}{\partial \bar{\xi}}
\end{aligned}$$

$$= \frac{\partial}{\partial \rho} + \frac{z_\sigma - \zeta}{\rho} \frac{\partial}{\partial \zeta} - \frac{7 \bar{\xi}}{6 \rho} \frac{\partial}{\partial \bar{\xi}} - \frac{z_\sigma - \zeta}{\rho} \frac{g'(\zeta)}{g(\zeta)} \bar{\xi} \frac{\partial}{\partial \bar{\xi}} \quad . \quad (10.3.39)$$

Inserting the previous identities into equation (10.3.33) we arrive at the following result for the correlation potential

$$\begin{aligned} v_{c,\sigma}^{GGA}(\rho, \zeta, \bar{\xi}) &= v_{c,\sigma}^{LDA}(\rho, \zeta) + H(\rho, \zeta, \bar{\xi}) + \rho \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \rho} \\ &\quad - (\zeta - z_\sigma) \left[\frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \zeta} - \frac{g'(\zeta)}{g(\zeta)} \bar{\xi}^2 \left\{ \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right\} \right] \\ &\quad + \frac{1}{6} \bar{\xi}^2 \left\{ \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right\} - \bar{\xi} \rho \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \rho \partial \bar{\xi}} \\ &\quad - \frac{1}{(2g(\zeta)k_S)^2 \rho} \nabla \rho \cdot \nabla \zeta \left[\frac{1}{\bar{\xi}} \frac{\partial^2 H(\rho, \zeta, \bar{\xi})}{\partial \zeta \partial \bar{\xi}} \right. \\ &\quad \quad \left. - \frac{g'(\zeta)}{g(\zeta)} \left(\frac{2}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right. \right. \\ &\quad \quad \quad \left. \left. + \bar{\xi} \frac{\partial}{\partial \bar{\xi}} \left\{ \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right\} \right) \right] \\ &\quad - \left[\frac{1}{(2g(\zeta)k_S)^3 \rho^2} \nabla |\nabla \rho| \cdot \nabla \rho - \frac{7}{6} \bar{\xi}^3 \right] \frac{\partial}{\partial \bar{\xi}} \left\{ \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right\} \\ &\quad - \frac{1}{(2g(\zeta)k_S)^2 \rho} \nabla^2 \rho \left\{ \frac{1}{\bar{\xi}} \frac{\partial H(\rho, \zeta, \bar{\xi})}{\partial \bar{\xi}} \right\} \quad , \quad (10.3.40) \end{aligned}$$

where we may still use the identity

$$\zeta - z_\sigma = z_\sigma (z_\sigma \zeta - 1) = z_\sigma \left(\frac{2\rho_\sigma}{\rho} - 2 \right) = -z_\sigma \frac{2\rho - \sigma}{\rho} \quad (10.3.41)$$

for the fourth term. Equation (10.3.40) is identical to equation (33) of Ref. [129] except for the sixth term on the right hand side, which was forgotten in the original work. However, it is included in the Fortran program distributed by J. Perdew.

A parametrization of the function $H(\rho, \zeta, \bar{\xi})$ has been first given by Perdew (PW91) [129] as $H = H_0 + H_1$ with

$$H_0 = 2g^3 \frac{\beta^2}{2\alpha} \ln \left[1 + \frac{2\alpha}{\beta} \frac{\bar{\xi}^2 + A\bar{\xi}^4}{1 + A\bar{\xi}^2 + A^2\bar{\xi}^4} \right] \quad , \quad (10.3.42)$$

where $\alpha = 0.09$, $\nu = 16(3/\pi)^{1/3} \approx 15.7559$, $C_c(0) = 0.004235$, $\beta = \nu C_c(0) \approx 0.066726$,

$$A = \frac{2\alpha}{\beta} \left(e^{-2\alpha \epsilon_c^{LDA}(\rho, \zeta) / (2g^3 \beta^2)} - 1 \right)^{-1} \quad , \quad (10.3.43)$$

and

$$H_1 = 2\nu \left[C_c(r_S) - C_c(0) - \frac{3}{7}C_x \right] g^3 \bar{\xi}^2 e^{-100g^4 \left(\frac{k_S^2}{k_F^2} \xi^2 \right)} , \quad (10.3.44)$$

$C_x = -0.001667$, $C_c(0) + \frac{3}{7}C_x = 0.003521$. The function $C_c(r_S)$ is given by a parametrization of Rasolt and Geldart [140] as

$$C_c(r_S) = C_{xc}(r_S) - C_x = \frac{c_1 + c_2 r_S + c_3 r_S^2}{1 + c_4 r_S + c_5 r_S^2 + c_6 r_S^3} - C_x , \quad (10.3.45)$$

where the coefficients are listed in Table 10.7. Note that we included a factor of

c_1	c_2	c_3	c_4	c_5	c_6
0.002568	0.023266	7.389×10^{-6}	8.723	0.472	7.389×10^{-2}

Table 10.7: Parameters for the Rasolt-Geldart parametrization of the function $C_{xc}(r_S)$.

two in front of the g^3 terms in equations (10.3.42) and (10.3.43) since Perdew and Wang used Hartree atomic units instead of Rydbergs.

Lateron, this approach was simplified by Perdew, Burke and Ernzerhof (PBE96) [130, 132], who omitted the term H_1 and proposed

$$H = 2g^3 \gamma \ln \left[1 + \frac{\beta}{\gamma} \frac{\bar{\xi}^2 + A\bar{\xi}^4}{1 + A\bar{\xi}^2 + A^2\bar{\xi}^4} \right] , \quad (10.3.46)$$

where

$$A = \frac{\beta}{\gamma} \left(e^{-\epsilon_c^{LDA}(\rho, \zeta)/(2g^3 \gamma)} - 1 \right)^{-1} , \quad (10.3.47)$$

and $\gamma = (1 - \ln 2)/\pi^2 \approx 0.031091$. The term H_0 originally given by Perdew reduces to equations (10.3.46)/(10.3.47) when we use $\gamma = \beta^2/(2\alpha) \approx 0.024735$. Note again the additional factor two. As for the exchange potential we defer the evaluation of the derivatives of the function H necessary to calculate the correlation potential to the Appendix A.1. However, since the correlation energy density enters the PW91 parametrization by Perdew and Wang as well as the newer one by Perdew, Burke and Ernzerhof we will need in addition the derivatives of this energy density with respect to both the density ρ and the spin polarization ζ , which we provide here. In doing so, we have to distinguish the spin interpolations given by von Barth and Hedin and by Vosko, Wilk and Nusair. In the former case, we start out from equation (10.1.33) and using the identity (10.1.16) in the form

$$\rho \frac{\partial \epsilon_c^i(\rho)}{\partial \rho} = \mu_c^i(\rho) - \epsilon_c^i(\rho) \quad \text{for } i = P, F , \quad (10.3.48)$$

we obtain

$$\rho \frac{\partial \epsilon_c(\rho, \zeta)}{\partial \rho} = \mu_c^P(\rho) - \epsilon_c^P(\rho) + [\mu_c^F(\rho) - \epsilon_c^F(\rho) - \mu_c^P(\rho) + \epsilon_c^P(\rho)] f(\zeta) \quad . \quad (10.3.49)$$

For the derivative with respect to ζ we obtain from equation (10.1.33)

$$\frac{\partial \epsilon_c(\rho, \zeta)}{\partial \zeta} = [\epsilon_c^F(\rho) - \epsilon_c^P(\rho)] \frac{df(\zeta)}{d\zeta} \quad , \quad (10.3.50)$$

where the derivative of the spin interpolation functions results from the definition (10.1.14) as

$$\frac{df(\zeta)}{d\zeta} = \frac{4}{3} \frac{(1+\zeta)^{1/3} - (1-\zeta)^{1/3}}{2^{4/3} - 2} \quad . \quad (10.3.51)$$

In case we want to apply the spin interpolation proposed by Vosko, Wilk and Nusair we start out from equation (10.1.63) and, again using the identity (10.3.48), we note

$$\begin{aligned} \rho \frac{\partial \epsilon_c(\rho, \zeta)}{\partial \rho} &= \mu_c^P(\rho) - \epsilon_c^P(\rho) + \frac{3}{\gamma} (\mu_c^S(\rho) - \epsilon_c^S(\rho)) (1 - \zeta^4) f(\zeta) \\ &\quad + [\mu_c^F(\rho) - \epsilon_c^F(\rho) - \mu_c^P(\rho) + \epsilon_c^P(\rho)] \zeta^4 f(\zeta) \quad . \quad (10.3.52) \end{aligned}$$

The derivative with respect to ζ is likewise easily formulated as

$$\begin{aligned} \frac{\partial \epsilon_c(\rho, \zeta)}{\partial \zeta} &= \frac{3}{\gamma} \epsilon_c^S(\rho) \left[-4\zeta^3 f(\zeta) + (1 - \zeta^4) \frac{df(\zeta)}{d\zeta} \right] \\ &\quad + [\epsilon_c^F(\rho) - \epsilon_c^P(\rho)] \left[4\zeta^3 f(\zeta) + \zeta^4 \frac{df(\zeta)}{d\zeta} \right] \quad . \quad (10.3.53) \end{aligned}$$

We close this section with a complete expression for the total energy for the generalized gradient approximation. Combining equations (10.1.6), (10.3.19), and (10.3.25) we note

$$\begin{aligned} E_{xc}[\rho, \zeta, \xi, \bar{\xi}] &= \int d^3\mathbf{r} \rho(\mathbf{r}) \epsilon_{xc}^{GGA}(\rho(\mathbf{r}), \zeta(\mathbf{r}), \xi(\mathbf{r}), \bar{\xi}(\mathbf{r})) \\ &= \frac{1}{2} \int d^3\mathbf{r} \rho \left\{ \epsilon_x^{P,LDA}(\rho) \left[\left(\frac{2\rho_\uparrow}{\rho} \right)^{4/3} F(\xi_\uparrow) + \left(\frac{2\rho_\downarrow}{\rho} \right)^{4/3} F(\xi_\downarrow) \right] \right. \\ &\quad \left. + \epsilon_c^{LDA}(\rho, \zeta) + H(\rho, \zeta, \bar{\xi}) \right\} \\ &= \frac{1}{2} \sum_\sigma \int d^3\mathbf{r} \rho \left\{ \epsilon_x^{P,LDA}(\rho) \left(\frac{2\rho_\sigma}{\rho} \right)^{4/3} F(\xi_\sigma) \right. \\ &\quad \left. + \epsilon_c^{LDA}(\rho, \zeta) + H(\rho, \zeta, \bar{\xi}) \right\} \quad . \quad (10.3.54) \end{aligned}$$

10.4 Self-interaction correction

In particular in the course of our discussion of Hartree-Fock theory we have, at several places, pointed to the exact cancellation of the electronic self-interaction in the combination of the Hartree and exchange terms. We used this property especially when we represented the respective potentials in Eqs. (6.1.13) and (6.1.14) in terms of the spin-dependent densities and density matrices rather than the single-particle orbitals. Nevertheless, already at that early stage we warned for any approximation to be done on only one of these two terms without taking care of a corresponding compensation in order to avoid a spurious self-interaction.

Of course, theories based on the density are predestinated for problems of the aforementioned kind and it is indeed the local density approximation to density functional theory, which violates the exact self-interaction cancellation. This is due to the fact that the exchange functional is approximated by the local density expression, whereas the exact form of the classical, Hartree potential is taken into consideration. While the consequences of this procedure remain somewhat small in metals, for which the approximation by a homogeneous electron gas is well justified, severe problems show up in inhomogeneous systems, in particular, semiconductors, insulators or systems with rather localized d or f electrons. Band gaps in such systems are usually underestimated by a factor of two and sometimes even missed.

In order to overcome such errors several researchers invented a new approach, which nowadays goes under the name self-interaction correction (SIC) and consists of a proper compensation of the errors introduced by the LDA. A good account of this approach has been given by Perdew and Zunger [136]. To be specific, we define an extra term in the total energy functional by

$$E_{SIC}[\rho] = \sum_{\alpha} \left[-\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_{\alpha;\sigma}(\mathbf{r})\rho_{\alpha;\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{3e^2}{4\pi} (6\pi^2)^{\frac{1}{3}} \sum_{\sigma} \int d^3\mathbf{r} \rho_{\alpha;\sigma}^{\frac{4}{3}}(\mathbf{r}) \right] , \quad (10.4.1)$$

where

$$\rho_{\alpha;\sigma}(\mathbf{r}) = |\chi_{\alpha;\sigma}(\mathbf{r})|^2 . \quad (10.4.2)$$

Obviously, this extra contribution consists of a sum over all single-particle states and subtracts for each state the self-interaction in both the Hartree and the exchange term. In other words, both contributions to the total energy are finally restored self-interaction free. This can be easily seen by comparing Eq. (10.4.1) to Eqs. (9.6.23) and (10.1.29). It should be noted that the SIC energy functional does not constitute an additional energy term but just corrects for erroneous terms contained in the total energy functional of density functional theory after the local density approximation has been done. Again this becomes clear from comparing the SIC functional to Eqs. (6.1.13) and (6.1.14).

With the definition of the SIC contribution to the energy functional at hand the SIC potential is readily calculated as

$$\begin{aligned}
 v_{xc,\alpha;\sigma}(\mathbf{r}) &= \frac{\delta E_{xc}[\rho]}{\delta \rho_{\alpha;\sigma}(\mathbf{r})} \\
 &= -\frac{e^2}{4\pi\epsilon_0} \sum_{\sigma'} \int d^3\mathbf{r}' \frac{\rho_{\alpha;\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{e^2}{\pi} (6\pi^2)^{\frac{1}{3}} \int d^3\mathbf{r} \rho_{\alpha;\sigma}^{\frac{1}{3}}(\mathbf{r}) \quad .
 \end{aligned}
 \tag{10.4.3}$$

It has to be added to the Kohn-Sham equations. While being clear in concept and simple in formulation the self-interaction correction nevertheless causes severe problems on implementation. These are due to the fact that the SIC potential explicitly depends on the orbital, the self-interaction of which has been removed. In other words, the Hamiltonian becomes orbital-dependent. As a consequence, wave functions are no longer orthogonal and the Kohn-Sham equations can no longer be formulated as a standard eigenvalue problem. Although the results of SIC calculations are indeed very promising the aforementioned severe difficulties have so far hindered more widespread use of this approach.

10.5 Exact exchange

While the need for an improved treatment especially of the exchange contribution to the total energy functional has become obvious from the discussion at the beginning of the previous section there exist several approaches to overcome the problems arising from the local exchange potential. A very promising idea was proposed already in the 1950'ties by Sharp and Horton [144] and, more recently, by Talman and Shadwick [160]. Their work has found widespread interest in the last decade and nowadays is summarized under the term "exact exchange". In short, the main idea consists of starting from the exact exchange energy functional as provided by Hartree-Fock theory and, by using the variational principle, mapping the exact nonlocal exchange potential onto a local potential. As a matter of fact this approach, like the self-interaction correction outlined in Sec. 10.4, resulted in much improved band gaps. Yet, the price is high. The complexity of the formalism substantially increases and the computer times are by a factor 20-30 higher as compared to the LDA treatment.

Nevertheless, the exact exchange approach is quite instructive and promising and thus will be the subject of the present section. To start with, we recall the total energy functional (6.1.7) of the Hartree-Fock method, which we write as

$$\begin{aligned}
 E &= \langle H_0 \rangle_{\psi} \\
 &= \sum_{\alpha} \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext,\sigma}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r})
 \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha\gamma} (1 - \delta_{\alpha\gamma}) \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\
& \quad \left[\frac{|\chi_{\alpha;\sigma'}(\mathbf{r}')|^2 |\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] \\
= & \sum_{\alpha} \sum_{\sigma} \int d^3\mathbf{r} \chi_{\alpha;\sigma}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext,\sigma}(\mathbf{r}) \right] \chi_{\alpha;\sigma}(\mathbf{r}) \\
& + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha\gamma} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \\
& \quad \left[\frac{|\chi_{\alpha;\sigma'}(\mathbf{r}')|^2 |\chi_{\gamma;\sigma'}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} - \frac{\chi_{\alpha;\sigma}^*(\mathbf{r}) \chi_{\gamma;\sigma'}^*(\mathbf{r}') \chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \right] ,
\end{aligned} \tag{10.5.1}$$

where we used the exact cancellation of the self-interaction term in the sum of the direct and exchange integral as well as the spin-dependent density and density matrix with the latter given by Eq. (5.7.17). In the functional (10.5.1) we identify the contributions due to the kinetic energy, external potential, classical Coulomb interaction, and the exchange contribution. As we have seen in Sec. 6.1 the Hartree-Fock equations are complicated integrodifferential equations, which are rather difficult to solve. As we have also seen, it is the exchange contribution, which makes things very involved. For this reason, improvements of this term were and still are desperately needed.

Following an idea of Slater, Sharp and Horton as well as Talman and Shadwick aimed at replacing the nonlocal potential coming with the Hartree-Fock approximation by an effective local potential. It would allow for a much simpler form of the single-particle equations. These authors suggested to calculate the desired effective local potential $v_{eff,\sigma}(\mathbf{r})$ variationally by inserting it into Schrödinger's equation and minimizing the total energy with respect to it. The variational problem is thus posed by

$$\begin{aligned}
\frac{\partial E}{\partial v_{eff,\sigma}(\mathbf{r})} = & \sum_{\alpha}^{occ} \sum_{\sigma'} \int d^3\mathbf{r}' \left[\frac{\partial E}{\partial \chi_{\alpha;\sigma'}^*(\mathbf{r}')} \frac{\partial \chi_{\alpha;\sigma'}(\mathbf{r}')}{\partial v_{eff,\sigma}(\mathbf{r})} \right. \\
& \left. + \frac{\partial E}{\partial \chi_{\alpha;\sigma'}(\mathbf{r}')} \frac{\partial \chi_{\alpha;\sigma'}^*(\mathbf{r}')}{\partial v_{eff,\sigma}(\mathbf{r})} \right] \stackrel{!}{=} 0 .
\end{aligned} \tag{10.5.2}$$

The variational derivative

$$\begin{aligned}
\frac{\partial E}{\partial \chi_{\alpha;\sigma'}^*(\mathbf{r}')} = & \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{eff,\sigma'}(\mathbf{r}') \right] \chi_{\alpha;\sigma'}(\mathbf{r}') \\
= & \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{ext,\sigma'}(\mathbf{r}') + v_H(\mathbf{r}') \right] \chi_{\alpha;\sigma'}(\mathbf{r}') \\
& - \frac{e^2}{4\pi\epsilon_0} \sum_{\gamma}^{occ} \sum_{\sigma''} \int d^3\mathbf{r}'' \frac{\chi_{\gamma;\sigma''}^*(\mathbf{r}'') \chi_{\gamma;\sigma'}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \chi_{\alpha;\sigma''}(\mathbf{r}'')
\end{aligned}$$

$$(10.5.3)$$

is just the left-hand side of the Hartree-Fock Eq. (6.1.11). In order to eliminate the kinetic energy operator we combine Eq. (10.5.3) with Schrödinger's equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff,\sigma'}(\mathbf{r}') - \varepsilon_\alpha \right] \chi_{\alpha;\sigma'}(\mathbf{r}') = 0 \quad (10.5.4)$$

and are thus able to write down the intermediate result

$$\begin{aligned} -\frac{\partial E}{\partial \chi_{\alpha;\sigma'}^*(\mathbf{r}')} &= \left[v_{eff,\sigma'}(\mathbf{r}') - v_{ext}(\mathbf{r}') - v_H(\mathbf{r}') - \varepsilon_\alpha \right] \chi_{\alpha;\sigma'}(\mathbf{r}') \\ &\quad + \frac{e^2}{4\pi\epsilon_0} \sum_{\gamma}^{occ} \sum_{\sigma''} \int d^3\mathbf{r}'' \frac{\chi_{\gamma;\sigma''}^*(\mathbf{r}'')\chi_{\gamma;\sigma'}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \chi_{\alpha;\sigma''}(\mathbf{r}'') \quad . \end{aligned} \quad (10.5.5)$$

The other variational derivative entering Eq. (10.5.2), the variational derivative of $\chi_{\alpha;\sigma'}^*(\mathbf{r}')$ with respect to $v_{eff,\sigma}(\mathbf{r})$, is calculated by perturbation theory. Using $\delta v_{eff,\sigma}(\mathbf{r})$ as a perturbation Schrödinger's equation reads as

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{eff,\sigma'}(\mathbf{r}') - \varepsilon_\alpha \right] \delta\chi_{\alpha;\sigma'}(\mathbf{r}') = [-\delta\varepsilon_\alpha + \delta v_{eff,\sigma'}(\mathbf{r}')] \chi_{\alpha;\sigma'}(\mathbf{r}') \quad , \quad (10.5.6)$$

with the first order correction to the single-particle wave function given by

$$\delta\chi_{\alpha;\sigma'}(\mathbf{r}') = \sum_{\sigma} \int d^3\mathbf{r} G_{\alpha;\sigma'\sigma}(\mathbf{r}', \mathbf{r}) \delta v_{eff,\sigma}(\mathbf{r}) \chi_{\alpha;\sigma}(\mathbf{r}) \quad , \quad (10.5.7)$$

where

$$G_{\alpha;\sigma'\sigma}(\mathbf{r}', \mathbf{r}) = \sum_{\beta \neq \alpha} \frac{\chi_{\beta;\sigma}^*(\mathbf{r})\chi_{\beta;\sigma'}(\mathbf{r}')}{\varepsilon_\alpha - \varepsilon_\beta} = G_{\alpha;\sigma\sigma'}^*(\mathbf{r}, \mathbf{r}') \quad . \quad (10.5.8)$$

From this we obtain

$$\frac{\partial \chi_{\alpha;\sigma'}^*(\mathbf{r}')}{\partial v_{eff,\sigma}(\mathbf{r})} = G_{\alpha;\sigma'\sigma}^*(\mathbf{r}', \mathbf{r}) \chi_{\alpha;\sigma}^*(\mathbf{r}) \quad . \quad (10.5.9)$$

Note that the expressions (10.5.7)/(10.5.8) are used here only to evaluate the variational derivative, hence, for an infinitesimally small perturbation, in which limit perturbation theory is exact.

Finally, combining Eqs. (10.5.2), (10.5.5) and (10.5.9) we arrive at the result

$$\begin{aligned} 0 &= \sum_{\alpha}^{occ} \sum_{\sigma'} \int d^3\mathbf{r}' \left(\left[v_{eff,\sigma'}(\mathbf{r}') - \varepsilon_\alpha - v_{ext,\sigma'}(\mathbf{r}') - v_H(\mathbf{r}') \right] \chi_{\alpha;\sigma'}(\mathbf{r}') \right. \\ &\quad \left. + \frac{e^2}{4\pi\epsilon_0} \sum_{\gamma}^{occ} \sum_{\sigma''} \int d^3\mathbf{r}'' \frac{\chi_{\gamma;\sigma''}^*(\mathbf{r}'')\chi_{\gamma;\sigma'}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \chi_{\alpha;\sigma''}(\mathbf{r}'') \right) \end{aligned}$$

$$\begin{aligned}
& \times G_{\alpha;\sigma'\sigma}^*(\mathbf{r}', \mathbf{r}) \chi_{\alpha;\sigma}^*(\mathbf{r}) \\
& + \sum_{\alpha}^{\text{occ}} \sum_{\sigma'} \int d^3 \mathbf{r}' \left(\left[v_{eff,\sigma'}(\mathbf{r}') - \varepsilon_{\alpha} - v_{ext,\sigma'}(\mathbf{r}') - v_H(\mathbf{r}') \right] \chi_{\alpha;\sigma'}^*(\mathbf{r}') \right. \\
& \quad \left. + \frac{e^2}{4\pi\epsilon_0} \sum_{\gamma}^{\text{occ}} \sum_{\sigma''} \int d^3 \mathbf{r}'' \frac{\chi_{\gamma;\sigma''}(\mathbf{r}'') \chi_{\gamma;\sigma'}^*(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \chi_{\alpha;\sigma''}^*(\mathbf{r}'') \right) \\
& \quad \times G_{\alpha;\sigma'\sigma}(\mathbf{r}', \mathbf{r}) \chi_{\alpha;\sigma}(\mathbf{r}) \quad .
\end{aligned} \tag{10.5.10}$$

Since $G_{\alpha;\sigma'\sigma}(\mathbf{r}', \mathbf{r})$ projects onto the subspace orthogonal to $\chi_{\alpha;\sigma}(\mathbf{r})$ and $\chi_{\alpha;\sigma}^*(\mathbf{r})$ the terms containing ε_{α} fall out and we are left with the result

$$\begin{aligned}
& \sum_{\sigma'} \int d^3 \mathbf{r}' \left[X_{\sigma}(\mathbf{r}', \mathbf{r}) + X_{\sigma}^*(\mathbf{r}', \mathbf{r}) \right] \\
& \quad \left[v_{eff,\sigma'}(\mathbf{r}') - v_{ext,\sigma'}(\mathbf{r}') - v_H(\mathbf{r}') \right] = Q(\mathbf{r}) \quad ,
\end{aligned} \tag{10.5.11}$$

where

$$\begin{aligned}
X_{\sigma}(\mathbf{r}', \mathbf{r}) & = \sum_{\alpha}^{\text{occ}} \sum_{\sigma'} \chi_{\alpha;\sigma'}(\mathbf{r}') G_{\alpha;\sigma'\sigma}^*(\mathbf{r}', \mathbf{r}) \chi_{\alpha;\sigma}^*(\mathbf{r}) \\
& = \sum_{\substack{\alpha,\beta \\ \alpha \neq \beta}}^{\text{occ}} \sum_{\sigma'} \frac{\chi_{\alpha;\sigma'}(\mathbf{r}') \chi_{\beta;\sigma}(\mathbf{r}) \chi_{\beta;\sigma'}^*(\mathbf{r}) \chi_{\alpha;\sigma}^*(\mathbf{r})}{\varepsilon_{\alpha} - \varepsilon_{\beta}} \\
& = X_{\sigma}^*(\mathbf{r}, \mathbf{r}')
\end{aligned} \tag{10.5.12}$$

and

$$\begin{aligned}
Q(\mathbf{r}) & = -\frac{e^2}{4\pi\epsilon_0} \sum_{\alpha\gamma}^{\text{occ}} \sum_{\sigma'\sigma''} \int d^3 \mathbf{r}' \int d^3 \mathbf{r}'' \\
& \quad \left[\frac{\chi_{\gamma;\sigma''}^*(\mathbf{r}'') \chi_{\gamma;\sigma'}(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \chi_{\alpha;\sigma''}(\mathbf{r}'') G_{\alpha;\sigma'\sigma}^*(\mathbf{r}', \mathbf{r}) \chi_{\alpha;\sigma}^*(\mathbf{r}) \right. \\
& \quad \left. + \frac{\chi_{\gamma;\sigma''}(\mathbf{r}'') \chi_{\gamma;\sigma'}^*(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}''|} \chi_{\alpha;\sigma''}^*(\mathbf{r}'') G_{\alpha;\sigma'\sigma}(\mathbf{r}', \mathbf{r}) \chi_{\alpha;\sigma}(\mathbf{r}) \right] \quad .
\end{aligned} \tag{10.5.13}$$

Note that the sum over β in Eq. (10.5.12) actually includes only the unoccupied states since each term in the sum is antisymmetric with respect to exchange of α and β .

As concerns interpretation of the just defined quantities we identify the difference of the potentials in square brackets on the left-hand side of Eq. (10.5.11) as the sought effective local exchange potential $v_{x,\sigma'}(\mathbf{r}')$. As expected,

it vanishes trivially when the exact, non-local exchange potential, which enters Eq. (10.5.11) via the quantity $Q(\mathbf{r})$, is set to zero. This latter function can be traced back to the last term in Eq. (10.5.3) and, hence, identified as the derivative of the exchange energy,

$$E_x = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\alpha\gamma} \sum_{\sigma\sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\chi_{\alpha;\sigma}^*(\mathbf{r})\chi_{\gamma;\sigma'}^*(\mathbf{r}')\chi_{\alpha;\sigma'}(\mathbf{r}')\chi_{\gamma;\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} , \quad (10.5.14)$$

with respect to the effective local potential,

$$Q(\mathbf{r}) = \frac{\partial E_x}{\partial v_{eff,\sigma}(\mathbf{r})} . \quad (10.5.15)$$

Combining this with Eq. (10.5.11) and writing the local effective exchange potential in the second square bracket on the left-hand side as the derivative of the exchange energy with respect to the charge density, hence,

$$\left[v_{eff,\sigma'}(\mathbf{r}') - v_{ext,\sigma'}(\mathbf{r}') - v_H(\mathbf{r}') \right] = \frac{\partial E_x}{\partial \rho_{\sigma'}(\mathbf{r}')} , \quad (10.5.16)$$

we obtain

$$\sum_{\sigma'} \int d^3\mathbf{r}' \left[X_{\sigma}(\mathbf{r}', \mathbf{r}) + X_{\sigma}^*(\mathbf{r}', \mathbf{r}) \right] \frac{\partial E_x}{\partial \rho_{\sigma'}(\mathbf{r}')} = \frac{\partial E_x}{\partial v_{eff,\sigma}(\mathbf{r})} . \quad (10.5.17)$$

Comparing this to Eq. (10.5.2) we are thus able to relate the quantity $X_{\sigma}(\mathbf{r}', \mathbf{r})$ as given by Eq. (10.5.12) to the derivative of the charge density with respect to the local effective potential, i.e.

$$X_{\sigma}(\mathbf{r}', \mathbf{r}) + X_{\sigma}^*(\mathbf{r}', \mathbf{r}) = \frac{\partial \rho(\mathbf{r}')}{\partial v_{eff,\sigma}(\mathbf{r})} . \quad (10.5.18)$$

In order to prepare for the discussion as well as further evaluation of the previous results we point to some important sum rules obeyed by $Q(\mathbf{r})$ and $X_{\sigma}(\mathbf{r}', \mathbf{r})$. They are based on the orthonormalization of the wave functions,

$$\int d^3\mathbf{r} \chi_{\beta;\sigma}^*(\mathbf{r})\chi_{\alpha;\sigma}(\mathbf{r}) = \delta_{\beta\alpha}; \stackrel{!}{=} 0 \quad \text{for } \alpha \neq \beta . \quad (10.5.19)$$

Since the double sum in the definition (10.5.12) of $X_{\sigma}(\mathbf{r}', \mathbf{r})$ excludes the term $\alpha = \beta$ we arrive at the sum rules

$$\int d^3\mathbf{r}' \left[X_{\sigma}(\mathbf{r}', \mathbf{r}) + X_{\sigma}^*(\mathbf{r}', \mathbf{r}) \right] = 0 \quad (10.5.20)$$

as well as

$$\int d^3\mathbf{r} \int d^3\mathbf{r}' \left[X_{\sigma}(\mathbf{r}', \mathbf{r}) + X_{\sigma}^*(\mathbf{r}', \mathbf{r}) \right] = \int d^3\mathbf{r} Q(\mathbf{r}) = 0 . \quad (10.5.21)$$

From these identities Görling recently draw the conclusion that inversion of the matrix $X_\sigma(\mathbf{r}', \mathbf{r})$ has to be preceded by proper exclusion of a constant potential [60]. However, as we will demonstrate next, the problem of a constant potential actually does never occur.

Of course, evaluation of the effective local exchange potential via Eqs. (10.5.11) to (10.5.13) depends on the actual representation of the wave function and thus must be worked out in detail for each particular calculational method. Nevertheless, it is useful to outline the general procedure for calculating the exact exchange potential already now.

To this end we start out by defining an basis of orthonormalized functions $|f_i(\mathbf{r})\rangle$,

$$\langle f_i(\mathbf{r}) | f_j(\mathbf{r}) \rangle = \delta_{ij} \quad , \quad (10.5.22)$$

which we use for the representation of products of wave functions,

$$\chi_{\beta;\sigma}^*(\mathbf{r})\chi_{\alpha;\sigma}(\mathbf{r}) = \sum_i C_{\beta\alpha;i} |f_i(\mathbf{r})\rangle \quad . \quad (10.5.23)$$

The expansion coefficients are calculated from

$$\int d^3\mathbf{r} f_i^*(\mathbf{r})\chi_{\beta;\sigma}^*(\mathbf{r})\chi_{\alpha;\sigma}(\mathbf{r}) = C_{\beta\alpha;i} \quad . \quad (10.5.24)$$

Comparing this to the identity (10.5.18) we realize that the basis set of the product wave functions does not comprise a constant function if only products with $\alpha \neq \beta$ are considered. Combining now Eqs. (10.5.12) and (10.5.22) we write

$$X_\sigma(\mathbf{r}', \mathbf{r}) + X_\sigma^*(\mathbf{r}', \mathbf{r}) = \sum_i \sum_j |f_i(\mathbf{r}')\rangle \alpha_{ij} \langle f_j(\mathbf{r})| \quad (10.5.25)$$

where

$$\alpha_{ij} = \sum_{\alpha;\sigma}^{occ} \sum_{\beta \neq \alpha} C_{\alpha;\beta i} \frac{1}{\varepsilon_\alpha - \varepsilon_\beta} C_{\alpha;\beta j}^* \quad . \quad (10.5.26)$$

Obviously, the matrix $X_\sigma(\mathbf{r}', \mathbf{r}) + X_\sigma^*(\mathbf{r}', \mathbf{r})$ acts like a projection operator onto the space spanned by the basis functions $|f_i(\mathbf{r})\rangle$ for the representation of the product wave functions. As a consequence, from Eq. (10.5.11) the effective local exchange potential is determined only within this space and, hence, can never comprise a constant contribution.

Finally, we formulate Eq. (10.5.11) as

$$\sum_i \sum_j |f_i(\mathbf{r}')\rangle \alpha_{ij} \langle f_j(\mathbf{r}) | v(\mathbf{r}) \rangle = |Q(\mathbf{r}')\rangle \quad (10.5.27)$$

hence

$$\sum_j \alpha_{ij} \langle f_j(\mathbf{r}) | v(\mathbf{r}) \rangle = \langle f_i(\mathbf{r}') | Q(\mathbf{r}') \rangle \quad . \quad (10.5.28)$$

Appendix A

Density functional theory: Details

A.1 GGA parametrizations

In the present section we complement the parametrizations for the functions $F(\xi)$ and $H(\rho, \zeta, \bar{\xi})$ entering the generalized gradient approximation with its first and second derivatives. They are needed for the calculation of the exchange and the correlation potential according to equations (10.3.20) and (10.3.40).

We start out with the parametrization of $F(\xi)$ given by Perdew and Wang (PW86) [134],

$$F(\xi) = (A(\xi))^m = (1 + a\xi^2/m + b\xi^4 + c\xi^6)^m, \quad (\text{A.1.1})$$

where $m = 1/15$, $a = 0.0864$, $b = 14$, and $c = 0.2$. From this we have

$$\begin{aligned} \frac{1}{\xi} \frac{d}{d\xi} F(\xi) &= m (A(\xi))^{m-1} B(\xi) \\ &= m (1 + a\xi^2/m + b\xi^4 + c\xi^6)^{m-1} (2a/m + 4b\xi^2 + 6c\xi^4), \end{aligned} \quad (\text{A.1.2})$$

and

$$\begin{aligned} \frac{d}{d\xi} \left\{ \frac{1}{\xi} \frac{d}{d\xi} F(\xi) \right\} &= m(m-1) (A(\xi))^{m-2} (B(\xi))^2 \xi + m (A(\xi))^{m-1} B'(\xi) \\ &= m(m-1) (1 + a\xi^2/m + b\xi^4 + c\xi^6)^{m-2} \\ &\quad \times (2a/m + 4b\xi^2 + 6c\xi^4)^2 \xi \\ &\quad + m (1 + a\xi^2/m + b\xi^4 + c\xi^6)^{m-1} (8b\xi + 24c\xi^3). \end{aligned} \quad (\text{A.1.3})$$

In the GGA-II parametrization proposed by Perdew and Wang (PW91) [128, 129, 133] the function $F(\xi)$ is given by

$$F(\xi) = \frac{A(\xi)}{B(\xi)} \quad , \quad (\text{A.1.4})$$

with

$$\begin{aligned} A(\xi) &= 1 + a_1 \xi \sinh^{-1}(a_2 \xi) + (a_3 - a_4 e^{-m\xi^2}) \xi^2 \\ &= 1 + a_1 \xi \ln \left(a_2 \xi + \sqrt{1 + a_2^2 \xi^2} \right) + (a_3 - a_4 e^{-m\xi^2}) \xi^2 \end{aligned} \quad (\text{A.1.5})$$

$$\begin{aligned} B(\xi) &= 1 + a_1 \xi \sinh^{-1}(a_2 \xi) + a_5 \xi^4 \\ &= 1 + a_1 \xi \ln \left(a_2 \xi + \sqrt{1 + a_2^2 \xi^2} \right) + a_5 \xi^4 \quad , \end{aligned} \quad (\text{A.1.6})$$

and the parameters listed in Table 10.5. For the first derivative with respect to ξ we write

$$\frac{d}{d\xi} F(\xi) = F(\xi) \left[\frac{A'(\xi)}{A(\xi)} - \frac{B'(\xi)}{B(\xi)} \right] \quad , \quad (\text{A.1.7})$$

where

$$\begin{aligned} A'(\xi) &= a_1 \ln \left(a_2 \xi + \sqrt{1 + a_2^2 \xi^2} \right) + a_1 a_2 \xi \frac{1}{\sqrt{1 + a_2^2 \xi^2}} \\ &\quad + 2\xi (a_3 - a_4 e^{-m\xi^2}) + 2\xi^3 a_4 m e^{-m\xi^2} \end{aligned} \quad (\text{A.1.8})$$

and

$$B'(\xi) = a_1 \ln \left(a_2 \xi + \sqrt{1 + a_2^2 \xi^2} \right) + a_1 a_2 \xi \frac{1}{\sqrt{1 + a_2^2 \xi^2}} + 4a_5 \xi^3 \quad . \quad (\text{A.1.9})$$

From this we obtain finally

$$\frac{1}{\xi} \frac{d}{d\xi} F(\xi) = \frac{1}{\xi} F(\xi) \left[\frac{A'(\xi)}{A(\xi)} - \frac{B'(\xi)}{B(\xi)} \right] \quad , \quad (\text{A.1.10})$$

and

$$\begin{aligned} \frac{d}{d\xi} \left\{ \frac{1}{\xi} \frac{d}{d\xi} F(\xi) \right\} &= \frac{1}{\xi} \frac{d}{d\xi} F(\xi) \left[\frac{A'(\xi)}{A(\xi)} - \frac{B'(\xi)}{B(\xi)} \right] - \frac{1}{\xi^2} F(\xi) \left[\frac{A'(\xi)}{A(\xi)} - \frac{B'(\xi)}{B(\xi)} \right] \\ &\quad + \frac{1}{\xi} F(\xi) \left[\frac{A''(\xi)}{A(\xi)} - \left(\frac{A'(\xi)}{A(\xi)} \right)^2 - \frac{B''(\xi)}{B(\xi)} + \left(\frac{B'(\xi)}{B(\xi)} \right)^2 \right] \\ &= \frac{1}{\xi} \frac{d}{d\xi} F(\xi) \left[\frac{A'(\xi)}{A(\xi)} - \frac{B'(\xi)}{B(\xi)} - \frac{1}{\xi} \right] \\ &\quad + \frac{1}{\xi} F(\xi) \left[\frac{A''(\xi)}{A(\xi)} - \left(\frac{A'(\xi)}{A(\xi)} \right)^2 - \frac{B''(\xi)}{B(\xi)} + \left(\frac{B'(\xi)}{B(\xi)} \right)^2 \right] \quad , \end{aligned} \quad (\text{A.1.11})$$

with

$$\begin{aligned}
A''(\xi) &= 2a_1a_2 \frac{1}{\sqrt{1+a_2^2\xi^2}} - a_1a_2\xi \frac{a_2^2\xi}{\left(\sqrt{1+a_2^2\xi^2}\right)^3} + 2\left(a_3 - a_4e^{-m\xi^2}\right) \\
&\quad + 4\xi^2a_4me^{-m\xi^2} + 6\xi^2a_4me^{-m\xi^2} - 4\xi^4a_4m^2e^{-m\xi^2} \\
&= a_1a_2 \frac{2+a_2^2\xi^2}{\left(\sqrt{1+a_2^2\xi^2}\right)^3} + 2\left(a_3 - a_4e^{-m\xi^2}\right) \\
&\quad + 10\xi^2a_4me^{-m\xi^2} - 4\xi^4a_4m^2e^{-m\xi^2}
\end{aligned} \tag{A.1.12}$$

and

$$B''(\xi) = a_1a_2 \frac{2+a_2^2\xi^2}{\left(\sqrt{1+a_2^2\xi^2}\right)^3} + 12a_5\xi^2 \quad . \tag{A.1.13}$$

The parametrization given by Engel and Vosko (EV93) [39], arising from a [3/3]-Padé approximation, is written as

$$F(\xi) = \frac{A(\xi^2)}{B(\xi^2)} \quad , \tag{A.1.14}$$

with

$$A(x) = 1 + a_1x^2 + a_2x^4 + a_3x^6 \tag{A.1.15}$$

and

$$B(x) = 1 + b_1x^2 + b_2x^4 + b_3x^6 \quad , \tag{A.1.16}$$

where

$$x = \xi^2 \quad , \quad \text{hence} \quad \frac{dx}{d\xi} = 2\xi \quad . \tag{A.1.17}$$

The coefficients entering this parametrization are given in Table 10.6. We thus obtain for the first derivative with respect to ξ

$$\frac{d}{d\xi}F(\xi) = \frac{dx}{d\xi} \frac{d}{dx} \frac{A(x)}{B(x)} = 2\xi F(\xi) \left[\frac{A'(x)}{A(x)} - \frac{B'(x)}{B(x)} \right] \quad , \tag{A.1.18}$$

with

$$A'(x) = a_1 + 2a_2x + 3a_3x^2 \tag{A.1.19}$$

and

$$B'(x) = b_1 + 2b_2x + 3b_3x^2 \quad . \tag{A.1.20}$$

Next we note

$$\frac{1}{\xi} \frac{d}{d\xi}F(\xi) = 2F(\xi) \left[\frac{A'(x)}{A(x)} - \frac{B'(x)}{B(x)} \right] \quad , \tag{A.1.21}$$

and thus finally arrive at

$$\begin{aligned}
\frac{d}{d\xi} \left\{ \frac{1}{\xi} \frac{d}{d\xi} F(\xi) \right\} &= 2 \frac{d}{d\xi} F(\xi) \left[\frac{A'(x)}{A(x)} - \frac{B'(x)}{B(x)} \right] + 2F(\xi) \frac{dx}{d\xi} \frac{d}{dx} \left[\frac{A'(x)}{A(x)} - \frac{B'(x)}{B(x)} \right] \\
&= 2\xi \left\{ \frac{1}{\xi} \frac{d}{d\xi} F(\xi) \right\} \left[\frac{A'(x)}{A(x)} - \frac{B'(x)}{B(x)} \right] \\
&\quad + 4\xi F(\xi) \left[\frac{A''(x)}{A(x)} - \left(\frac{A'(x)}{A(x)} \right)^2 - \frac{B''(x)}{B(x)} + \left(\frac{B'(x)}{B(x)} \right)^2 \right]
\end{aligned} \tag{A.1.22}$$

with

$$A''(x) = 2a_2 + 6a_3 x \tag{A.1.23}$$

and

$$B''(x) = 2b_2 + 6b_3 x \quad . \tag{A.1.24}$$

Last but not least the parametrization by Perdew, Burke and Ernzerhof (PBE96) [130, 132] is given by

$$F(\xi) = 1 + \kappa - \frac{\kappa}{1 + \mu \xi^2 / \kappa} \quad , \tag{A.1.25}$$

where $\kappa = 0.804$ and $\mu = 0.21951$. Hence,

$$\frac{d}{d\xi} F(\xi) = \frac{2\mu\xi}{(1 + \mu \xi^2 / \kappa)^2} \quad , \tag{A.1.26}$$

$$\frac{1}{\xi} \frac{d}{d\xi} F(\xi) = \frac{2\mu}{(1 + \mu \xi^2 / \kappa)^2} \quad , \tag{A.1.27}$$

and

$$\frac{d}{d\xi} \left\{ \frac{1}{\xi} \frac{d}{d\xi} F(\xi) \right\} = - \frac{8\mu^2 \xi / \kappa}{(1 + \mu \xi^2 / \kappa)^3} \quad . \tag{A.1.28}$$

For the determination of the gradient correction to the correlation energy density and potential we start out discussing the parametrization given by Perdew, Burke and Ernzerhof (PBE96) [130, 132],

$$H = 2g^3 \gamma \ln \left[1 + \frac{\beta}{\gamma} \frac{\bar{\xi}^2 + A\bar{\xi}^4}{1 + A\bar{\xi}^2 + A^2\bar{\xi}^4} \right] \quad , \tag{A.1.29}$$

where

$$A = \frac{\beta}{\gamma} \left(e^{-\epsilon_c^{LDA}(\rho, \zeta) / (2g^3 \gamma)} - 1 \right)^{-1} \quad , \tag{A.1.30}$$

and $\gamma = (1 - \ln 2) / \pi^2 \approx 0.031091$. Here $g(\zeta)$ is the spin interpolation function defined by equation (10.3.27). The term H_0 originally given by Perdew reduces

to equations (10.3.45)/(10.3.46) when we use $\gamma = \beta^2/(2\alpha) \approx 0.024735$. From these specifications we easily derive

$$\frac{\partial A}{\partial \rho} = \frac{\beta}{\gamma} \frac{1}{2g^3\gamma} \frac{\partial \epsilon_c^{LDA}}{\partial \rho} \frac{e^{-\epsilon_c^{LDA}/(2g^3\gamma)}}{(e^{-\epsilon_c^{LDA}(\rho,\zeta)/(2g^3\gamma)} - 1)^2} = \frac{A^2}{2g^3\beta} E \frac{\partial \epsilon_c^{LDA}}{\partial \rho} \quad (\text{A.1.31})$$

and

$$\begin{aligned} \frac{\partial A}{\partial \zeta} &= \frac{\beta}{\gamma} \frac{\frac{\partial \epsilon_c^{LDA}}{\partial \zeta} 2g^3\gamma - \epsilon_c^{LDA} 6g'g^2\gamma}{(2g^3\gamma)^2} \frac{e^{-\epsilon_c^{LDA}/(2g^3\gamma)}}{(e^{-\epsilon_c^{LDA}(\rho,\zeta)/(2g^3\gamma)} - 1)^2} \\ &= \frac{A^2}{2g^3\beta} E \left(\frac{\partial \epsilon_c^{LDA}}{\partial \zeta} - 3\epsilon_c^{LDA} \frac{g'}{g} \right) , \end{aligned} \quad (\text{A.1.32})$$

where we have abbreviated

$$E = e^{-\epsilon_c^{LDA}/(2g^3\gamma)} = 1 + \frac{\beta}{\gamma} \frac{1}{A} . \quad (\text{A.1.33})$$

In addition, we calculate the derivative of the spin interpolation function (10.3.27) as

$$\frac{dg(\zeta)}{d\zeta} = \frac{1}{3} \left[(1+\zeta)^{-1/3} - (1-\zeta)^{-1/3} \right] \quad (\text{A.1.34})$$

Next we define

$$B = \frac{a}{b} = \frac{x + Ax^2}{1 + Ax + A^2x^2} , \quad (\text{A.1.35})$$

for $x = \bar{\xi}^2$ and obtain

$$\frac{\partial B}{\partial x} = B \left(\frac{a_x}{a} - \frac{b_x}{b} \right) \quad (\text{A.1.36})$$

with

$$a_x = \frac{\partial a}{\partial x} = 1 + 2Ax , \quad b_x = \frac{\partial b}{\partial x} = A + 2A^2x = Aa_x , \quad (\text{A.1.37})$$

hence

$$\frac{\partial B}{\partial x} = Ba_x \left(\frac{1}{a} - \frac{A}{b} \right) = \frac{a_x}{b^2} . \quad (\text{A.1.38})$$

In addition, we note

$$\frac{\partial B}{\partial A} = B \left(\frac{a_A}{a} - \frac{b_A}{b} \right) \quad (\text{A.1.39})$$

with

$$a_A = \frac{\partial a}{\partial A} = x^2 , \quad b_A = \frac{\partial b}{\partial A} = x + 2Ax^2 = xa_x , \quad (\text{A.1.40})$$

hence

$$\frac{\partial B}{\partial A} = -\frac{Ax^3}{b^2} (2 + Ax) \quad (\text{A.1.41})$$

From the previous identities we have

$$\begin{aligned}
\frac{\partial H}{\partial \rho} &= 2g^3 \gamma \frac{\frac{\beta}{\gamma} \frac{\partial B}{\partial A} \frac{\partial A}{\partial \rho}}{1 + \frac{\beta}{\gamma} B} \\
&= 2g^3 \beta \frac{1}{1 + \frac{\beta}{\gamma} B} B \left(\frac{a_A}{a} - \frac{b_A}{b} \right) \frac{A^2}{2g^3 \beta} E \frac{\partial \epsilon_c^{LDA}}{\partial \rho} \\
&= BA^2 \frac{1}{1 + \frac{\beta}{\gamma} B} \left(\frac{a_A}{a} - \frac{b_A}{b} \right) E \frac{\partial \epsilon_c^{LDA}}{\partial \rho} \quad , \quad (A.1.42)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial H}{\partial \zeta} &= 6g^2 g' \gamma \ln \left[1 + \frac{\beta}{\gamma} B \right] + 2g^3 \gamma \frac{\frac{\beta}{\gamma} \frac{\partial B}{\partial A} \frac{\partial A}{\partial \zeta}}{1 + \frac{\beta}{\gamma} B} \\
&= 3 \frac{g'}{g} H + 2g^3 \beta \frac{1}{1 + \frac{\beta}{\gamma} B} B \left(\frac{a_A}{a} - \frac{b_A}{b} \right) \frac{A^2}{2g^3 \beta} E \left(\frac{\partial \epsilon_c^{LDA}}{\partial \zeta} - 3\epsilon_c^{LDA} \frac{g'}{g} \right) \\
&= 3 \frac{g'}{g} H + BA^2 \frac{1}{1 + \frac{\beta}{\gamma} B} \left(\frac{a_A}{a} - \frac{b_A}{b} \right) E \left(\frac{\partial \epsilon_c^{LDA}}{\partial \zeta} - 3\epsilon_c^{LDA} \frac{g'}{g} \right) \quad , \quad (A.1.43)
\end{aligned}$$

and

$$\frac{\partial H}{\partial \xi} = 2g^3 \gamma \frac{\frac{\beta}{\gamma} 2\bar{\xi} \frac{\partial B}{\partial x}}{1 + \frac{\beta}{\gamma} B} = 2g^3 \beta \frac{1}{1 + \frac{\beta}{\gamma} B} 2\bar{\xi} B a_x \left(\frac{1}{a} - \frac{A}{b} \right) \quad . \quad (A.1.44)$$

Defining

$$\Lambda = B \frac{1}{1 + \frac{\beta}{\gamma} B} \left(\frac{a_A}{a} - \frac{b_A}{b} \right) = \frac{1}{1 + \frac{\beta}{\gamma} B} \frac{\partial B}{\partial A} = \Lambda(\bar{\xi}) \quad (A.1.45)$$

we note

$$\frac{\partial H}{\partial \rho} = A^2 \Lambda E \frac{\partial \epsilon_c^{LDA}}{\partial \rho} \quad (A.1.46)$$

and

$$\frac{\partial H}{\partial \zeta} = 3 \frac{g'}{g} H + A^2 \Lambda E \left(\frac{\partial \epsilon_c^{LDA}}{\partial \zeta} - 3\epsilon_c^{LDA} \frac{g'}{g} \right) \quad . \quad (A.1.47)$$

From equation (A.1.45) we evaluate

$$\begin{aligned}
\frac{\partial \Lambda}{\partial \bar{\xi}} &= 2\bar{\xi} \frac{1}{1 + \frac{\beta}{\gamma} B} \frac{\partial^2 B}{\partial x \partial A} - 2\bar{\xi} \frac{1}{(1 + \frac{\beta}{\gamma} B)^2} \frac{\beta}{\gamma} \frac{\partial B}{\partial x} \frac{\partial B}{\partial A} \\
&= 2\bar{\xi} \frac{1}{(1 + \frac{\beta}{\gamma} B)^2} \left[\frac{\partial^2 B}{\partial x \partial A} + \frac{\beta}{\gamma} \left(B \frac{\partial^2 B}{\partial x \partial A} - \frac{\partial B}{\partial x} \frac{\partial B}{\partial A} \right) \right] \quad . \quad (A.1.48)
\end{aligned}$$

Using

$$a_{Ax} = \frac{\partial^2 a}{\partial A \partial x} = 2x \quad , \quad b_{Ax} = \frac{\partial^2 b}{\partial A \partial x} = 1 + 4Ax \quad (A.1.49)$$

as well as equations (A.1.37), (A.1.38) and (A.1.40) we write

$$\frac{\partial^2 B}{\partial A \partial x} = \frac{a_{Ax}b^2 - a_x 2bb_A}{b^4} = \frac{2xb(b - a_x^2)}{b^4} = \frac{-6Axab}{b^4} . \quad (\text{A.1.50})$$

Combining this with equations (A.1.37), (A.1.38) and (A.1.41) we arrive at

$$\begin{aligned} B \frac{\partial^2 B}{\partial A \partial x} - \frac{\partial B}{\partial x} \frac{\partial B}{\partial A} &= \frac{1}{b^4} [-6Axa^2 + (1 + 2Ax)Ax^3(2 + Ax)] \\ &= \frac{-Ax}{b^4} [6a^2 - x^2(2 + 5Ax + 2A^2x^2)] \\ &= \frac{-Ax}{b^4} [6a^2 + bx^2 - 3(x^2 + 2Ax^3 + A^2x^4)] \\ &= \frac{-Ax}{b^4} [3a^2 + bx^2] . \end{aligned} \quad (\text{A.1.51})$$

We thus collect the identities (A.1.48), (A.1.50) and (A.1.51) and obtain

$$\frac{1}{\xi} \frac{\partial \Lambda}{\partial \xi} = -2 \frac{Ax}{b^4} \frac{1}{(1 + \frac{\beta}{\gamma} B)^2} \left[6ab + \frac{\beta}{\gamma} (3a^2 + bx^2) \right] . \quad (\text{A.1.52})$$

We are thus in a position to write the second derivatives as

$$\frac{1}{\xi} \frac{\partial^2 H}{\partial \rho \partial \xi} = A^2 \frac{1}{\xi} \frac{\partial \Lambda}{\partial \xi} E \frac{\partial \epsilon_c^{LDA}}{\partial \rho} \quad (\text{A.1.53})$$

and

$$\frac{1}{\xi} \frac{\partial^2 H}{\partial \zeta \partial \xi} = 3 \frac{g'}{g} \frac{1}{\xi} \frac{\partial H}{\partial \xi} + A^2 \frac{1}{\xi} \frac{\partial \Lambda}{\partial \xi} E \left(\frac{\partial \epsilon_c^{LDA}}{\partial \zeta} - 3 \epsilon_c^{LDA} \frac{g'}{g} \right) . \quad (\text{A.1.54})$$

For the second derivative of H with respect to ξ we start from equation (A.1.44) and write

$$\begin{aligned} \frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial H}{\partial \xi} \right\} &= \frac{\partial}{\partial \xi} \left\{ 4g^3 \beta \frac{1}{1 + \frac{\beta}{\gamma} B} \frac{\partial B}{\partial x} \right\} \\ &= 2g^3 \beta (4\bar{\xi}) \left[\frac{1}{1 + \frac{\beta}{\gamma} B} \frac{\partial^2 B}{\partial x^2} - \frac{1}{(1 + \frac{\beta}{\gamma} B)^2} \frac{\beta}{\gamma} \left(\frac{\partial B}{\partial x} \right)^2 \right] \\ &= 2g^3 \beta (4\bar{\xi}) \frac{1}{(1 + \frac{\beta}{\gamma} B)^2} \left[\frac{\partial^2 B}{\partial x^2} + \frac{\beta}{\gamma} \left(B \frac{\partial^2 B}{\partial x^2} - \left(\frac{\partial B}{\partial x} \right)^2 \right) \right] . \end{aligned} \quad (\text{A.1.55})$$

Using

$$a_{xx} = \frac{\partial^2 a}{\partial x^2} = 2A \quad , \quad b_{xx} = \frac{\partial^2 b}{\partial x^2} = 2A^2 = Aa_{xx} \quad (\text{A.1.56})$$

as well as equations (A.1.37) and (A.1.38) we obtain

$$\frac{\partial^2 B}{\partial x^2} = \frac{a_{xx}b^2 - a_x 2bb_x}{b^4} = \frac{2Ab(b - a_x^2)}{b^4} = \frac{-6A^2ab}{b^4} \quad , \quad (\text{A.1.57})$$

and this results in

$$\begin{aligned} B \frac{\partial^2 B}{\partial x^2} - \left(\frac{\partial B}{\partial x} \right)^2 &= \frac{1}{b^4} [-6A^2a^2 - a_x^2] = \frac{1}{b^4} [-6A^2a^2 - 4Aa - 1] \\ &= -\frac{1}{b^4} [3 - 8b + 6b^2] \quad . \end{aligned} \quad (\text{A.1.58})$$

Inserting this into equation (A.1.55) we arrive at

$$\frac{\partial}{\partial \xi} \left\{ \frac{1}{\xi} \frac{\partial H}{\partial \xi} \right\} = -2g^3\beta(4\bar{\xi}) \frac{1}{b^4} \frac{1}{(1 + \frac{\beta}{\gamma}B)^2} \left[6A^2ab + \frac{\beta}{\gamma}(3 - 8b + 6b^2) \right] \quad . \quad (\text{A.1.59})$$

As already mentioned in section 10.3 the functional form of the H as given by Perdew, Burke and Ernzerhof had been proposed before by Perdew and Wang with slightly different parameters. In addition, these authors included a second term. Just to be complete, Perdew and Wang proposed $H = H_0 + H_1$ with H_0 given by equations (10.3.42) and (10.3.43) or alternatively by equations (A.1.29) and (A.1.30) with $\gamma = \beta^2/(2\alpha) \approx 0.024735$. The second term has the form

$$H_1 = 2\nu \left[C_c(r_S) - C_c(0) - \frac{3}{7}C_x \right] g^3 \bar{\xi}^2 e^{-\bar{E}} \quad , \quad (\text{A.1.60})$$

where

$$C_c(r_S) = C_{xc}(r_S) - C_x = \frac{c_1 + c_2 r_S + c_3 r_S^2}{1 + c_4 r_S + c_5 r_S^2 + c_6 r_S^3} - C_x =: \frac{C}{D} - C_x \quad , \quad (\text{A.1.61})$$

with the coefficients listed in Table 10.7. In addition, using equation (10.3.28) as well as the identity

$$\frac{4}{\pi k_F} = \frac{4}{\pi(3\pi^2\rho)^{1/3}} = \left(\frac{16}{3\pi^2} \right)^{\frac{2}{3}} r_S \quad , \quad (\text{A.1.62})$$

which follows from combining equations (10.1.20) and (10.1.21), we abbreviated

$$\bar{E} = 100g^4 \frac{4}{\pi k_F} \bar{\xi}^2 = 100g^4 \bar{\xi}^2 \left(\frac{16}{3\pi^2} \right)^{\frac{2}{3}} r_S \quad . \quad (\text{A.1.63})$$

From equation (10.1.22) we obtain

$$\rho \frac{dC_c(r_S)}{d\rho} = -\frac{1}{3}r_S \frac{dC_c(r_S)}{dr_S} = -\frac{1}{3}r_S \frac{C'D - CD'}{D^2} \quad , \quad (\text{A.1.64})$$

where

$$C' = \frac{dC}{dr_S} = c_2 + 2c_3 r_S \quad , \quad D' = \frac{dD}{dr_S} = c_4 + 2c_5 r_S + 3c_6 r_S^2 \quad . \quad (\text{A.1.65})$$

The derivatives of \bar{E} are easily evaluated as

$$\rho \frac{\partial \bar{E}}{\partial \rho} = -\frac{1}{3} \bar{E} \quad , \quad (\text{A.1.66})$$

$$\frac{\partial \bar{E}}{\partial \zeta} = 4 \frac{g'}{g} \bar{E} \quad , \quad (\text{A.1.67})$$

$$\frac{\partial \bar{E}}{\partial \xi} = \frac{2}{\xi} \bar{E} \quad , \quad (\text{A.1.68})$$

and we thus obtain

$$\rho \frac{\partial H_1}{\partial \rho} = 2\nu \rho \frac{dC_c}{d\rho} g^3 \bar{\xi}^2 e^{-\bar{E}} + \frac{1}{3} H_1 \bar{E} \quad , \quad (\text{A.1.69})$$

$$\frac{\partial H_1}{\partial \zeta} = H_1 \frac{g'}{g} [3 - 4\bar{E}] \quad , \quad (\text{A.1.70})$$

$$\frac{\partial H_1}{\partial \xi} = \frac{2}{\xi} H_1 [1 - \bar{E}] \quad . \quad (\text{A.1.71})$$

This leads to the following results for the second derivatives

$$\begin{aligned} \frac{1}{\bar{\xi}} \rho \frac{\partial^2 H_1}{\partial \rho \partial \bar{\xi}} &= \frac{2}{\bar{\xi}^2} \rho \frac{\partial}{\partial \rho} \{ H_1 [1 - \bar{E}] \} \\ &= \frac{2}{\bar{\xi}^2} 2\nu \rho \frac{dC_c}{d\rho} g^3 \bar{\xi}^2 e^{-\bar{E}} [1 - \bar{E}] + \frac{2}{3\bar{\xi}^2} H_1 \bar{E} [1 - \bar{E}] + \frac{2}{3\bar{\xi}^2} H_1 \bar{E} \\ &= 4\nu \rho \frac{dC_c}{d\rho} g^3 e^{-\bar{E}} [1 - \bar{E}] + \frac{2}{3\bar{\xi}^2} H_1 \bar{E} [2 - \bar{E}] \quad , \quad (\text{A.1.72}) \end{aligned}$$

$$\begin{aligned} \frac{1}{\bar{\xi}} \frac{\partial^2 H_1}{\partial \zeta \partial \bar{\xi}} &= \frac{2}{\bar{\xi}^2} \frac{\partial}{\partial \zeta} \{ H_1 [1 - \bar{E}] \} \\ &= \frac{2}{\bar{\xi}^2} H_1 \frac{g'}{g} [3 - 4\bar{E}] [1 - \bar{E}] - \frac{2}{\bar{\xi}^2} H_1 4 \frac{g'}{g} \bar{E} \\ &= \frac{2}{\bar{\xi}^2} H_1 \frac{g'}{g} [3 - 11\bar{E} + 4\bar{E}^2] \quad , \quad (\text{A.1.73}) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial \xi} \left\{ \frac{1}{\bar{\xi}} \frac{\partial H_1}{\partial \bar{\xi}} \right\} &= \frac{\partial}{\partial \xi} \left\{ \frac{2}{\bar{\xi}^2} H_1 [1 - \bar{E}] \right\} \\ &= -\frac{4}{\bar{\xi}^3} H_1 [1 - \bar{E}] + \frac{2}{\bar{\xi}^2} \frac{2}{\xi} H_1 [1 - \bar{E}]^2 - \frac{2}{\bar{\xi}^2} H_1 \frac{2}{\xi} \bar{E} \\ &= -\frac{4}{\bar{\xi}^3} H_1 \bar{E} (2 - \bar{E}) \quad . \quad (\text{A.1.74}) \end{aligned}$$

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