Density Functional Theory for Superconductors:
A first principles approach to the superconducting phase

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## Contents

1 Introduction 3

2 Basic theorems 6
   2.1 Hamiltonian ........................................ 6
   2.2 Hohenberg-Kohn theorem .......................... 7
   2.3 Kohn-Sham system ................................ 10
   2.4 KS equation for the ions – KS phonons .......... 12
   2.5 KS-Bogoliubov-de Gennes equations .............. 15
   2.6 Decoupling approximation – KS gap equation .... 16
   2.7 The exact linearized gap equation ............... 20

3 Perturbation expansion for the xc terms 23
   3.1 Unperturbed system ................................ 23
   3.2 Harmonic expansion around the equilibrium ...... 24
   3.3 Many-body perturbation theory .................... 27
   3.4 Feynman rules ...................................... 30
   3.5 Lowest order terms ................................ 35
   3.6 Random Phase Approximation ..................... 38
   3.7 Exchange-correlation potentials .................. 40
   3.8 Effective interaction .............................. 45

4 The LMTO method 46
   4.1 Introduction ........................................ 46
   4.2 The basis functions and the ASA-Hamiltonian .... 47
   4.3 Sketch of a calculation ............................ 50
   4.4 The wave functions ................................ 51

5 The Coulomb interaction 53
   5.1 LMTO-ASA representation ......................... 53
   5.2 Product basis method .............................. 56

6 Results: Coulomb interaction 58
   6.1 Aluminum .......................................... 58
   6.2 Niobium ............................................ 64
### CONTENTS

7 Results: phonon-mediated interaction  71
  7.1 Material-independent properties  71
  7.2 Simple metals  75

8 Conclusion  80

A Exact properties of the pairing potential matrix-elements  82
  A.1 Translation  83
  A.2 Rotation  83
  A.3 Particle Interchange  85
  A.4 Time-Reversal Symmetry  86

B Definition of the Green's functions  87

C Prefactors from Wick's theorem  91
  C.1 Diagrams without pair potentials  91
  C.2 Diagrams with pair potentials  93

D Evaluation of the first order diagrams  95

E Evaluation of the Matsubara sums  103

Bibliography  105

Zusammenfassung  108

Danksagung  112

Lebenslauf  114

Publikationen  115
Chapter 1

Introduction

After the discovery of superconductivity in 1911 by H. Kamerlingh Onnes [1] it took more than 40 years until the phenomenon was understood on a microscopic basis. Bardeen, Cooper and Schrieffer gave a description of the superconducting state [2] in terms of condensed Cooper pairs. This theory was motivated by Coopers observation that the normal state of an electron gas in the presence of an attractive interaction is unstable against the formation of electron pairs [3]. The source of the attractive interaction among the electrons was found to be the coupling of the electrons to the phonons of the system [4]. An effective electron-electron interaction was derived, up to first order in the electron-phonon coupling, by Fröhlich [5] and Bardeen and Pines [6]. In the BCS theory a simplified model for this interaction was used. This theory is very successful in the description of the universal properties of superconductors, i.e., those properties which all conventional superconductors have in common. An example for such a property is the scaled gap \( \Delta / \Delta_0 \) as a function of \( T / T_c \). For material-specific properties such as the critical temperature \( T_c \) itself, the BCS model gives only very rough estimates. Also, the BCS model is limited to the weak-coupling regime, which further reduces the range of applicability.

Some of these drawbacks were cured by the Eliashberg theory [7, 8, 9]. This is basically a generalization of Migdal’s theory of electron-phonon coupling in metals [10] to the superconducting state, using Nambu’s Green’s function formulation [11]. In this theory the Dyson equation is considered with an approximate self-energy, which takes into account the first-order diagrams with respect to the phonon propagator. This approximation is justified by Migdal’s theorem, which states that vertex corrections with respect to the phonon propagator can be neglected. Due to the separation of the energy scales in a superconductor – the energy of the superconducting gap is usually 2 - 3 orders of magnitude smaller than the typical electronic energies, like, e.g., the Fermi energy – the problem can be split into a low-energy problem, treating the superconducting properties, and a high-energy problem which attacks the Coulomb-interacting electrons in a fixed potential. The Eliashberg theory, together with band structure theory, provides the basic ingredients to a first-principles theory of superconductors [12]. However, there is still the value of the so-called Coulomb
pseudo-potential $\mu^*$ which cannot be calculated rigorously and which is mostly fitted to experimental data.

One very successful method for first-principles calculations in a variety of different fields, ranging from chemistry over materials sciences to biological systems, is density-functional theory (DFT). It is based on the Hohenberg-Kohn (HK) theorem [13] which states that the electronic density alone determines the whole physics of a system, and the Kohn-Sham (KS) scheme [14] which maps the interacting system onto an auxiliary non-interacting system with the same density. All many-body aspects of the problem are shifted into the construction of the exchange-correlation (xc) functional, which is unique and universal, i.e., it has the same functional dependence on the density for all materials. Oliveira, Gross and Kohn (OGK) [15] extended the DFT to superconducting systems by including the superconducting order parameter as a further “density”. This is done in analogy to the formulation of DFT for magnetic systems where the magnetization, the order parameter of the ferromagnetic state, is treated as additional “density”. The nature of the attractive electron-electron interaction was not specified in this work. Kurth and Gross developed a functional, based on first-order perturbation theory in the superconducting state [16, 17, 18], using the Bardeen-Pines interaction [6] as model for the attractive interaction. Similar to the above mentioned works, the inclusion of the Bardeen-Pines interaction cannot be justified on rigorous grounds and limits the applicability of the method to weak-coupling superconductors.

The main task of the present work is to formulate a rigorous first principles method which allows the calculation and prediction of superconducting properties of materials, including the strong-coupling case. To this end the OGK formulation of DFT for superconductors is combined with the DFT for multicomponent systems, treating the electron-ion system [19, 20, 21]. This leads to an in principle exact description of a superconducting electron-ion system. In chapter 2 the system considered is defined in terms of its Hamiltonian. The new DFT formulation is established by first proving the Hohenberg-Kohn theorem, and then defining the Kohn-Sham systems for the ions and the electrons. The ionic KS equation, which is a two-body Schrödinger equation, can be solved in terms of its collective modes, i.e., the KS phonons, which are a well-defined concept. The electrons are, as in the OGK formulation, described by KS-Bogoliubov-de Gennes equations which can, in a certain approximation, be decoupled into their high-energy and their low-energy parts. The latter gives rise to a generalized gap equation while the former reduces to the ordinary KS problem of the normal state. In chapter 3 an approximation for the xc energy functional and the xc pair potential will be developed. For this purpose we will employ Kohn-Sham perturbation theory [17, 18] and generalize the Feynman rules for a diagrammatic expansion of the xc energy. The electron-phonon interaction will be treated in a similar way as in the Eliashberg theory, i.e., the first-order terms with respect to the phonon propagator will be taken into account. In this way, effects due to the retardation of the phonons are treated properly. For the
Coulomb interaction we will, in addition to the first-order functional, also develop an approximation similar to an RPA. The central result of this chapter will be the effective interaction appearing in the KS gap equation. This quantity can supply information about the mechanism of superconductivity in a given material. The next chapter gives a brief overview over the LMTO-ASA method, which is then used for the actual calculations in this work. Chapter 5 describes how the Coulombic part of the effective interaction in the gap equation can be treated numerically and chapter 6 discusses its properties. It will be shown, that the first-order approximation for the Coulomb interaction is not sufficient, but that the RPA gives physical results. Chapter 7 describes the phononic part of the effective interaction.
Chapter 2

Basic theorems

2.1 Hamiltonian

To establish a first principles theory of superconductivity, including a phonon induced mechanism, one has to treat the phonons in a consistent way. This can be achieved, when the theory is based on the full electron-ion problem, which is described by the following Hamiltonian\(^1\):

\[
\hat{H} = (\hat{T}^e + \hat{U}^{ee} + \hat{V}^e) + (\hat{T}^i + \hat{U}^{ii}) + \hat{U}^{ei} + \hat{\Delta} - \mu \hat{N} \tag{2.1}
\]

with the electronic contributions

\[
\hat{T}^e = \sum_\sigma \int d^3r \; \hat{\Psi}_{\sigma}^\dagger (r) \left( -\frac{\nabla^2}{2} \right) \hat{\Psi}_{\sigma} (r) \tag{2.2}
\]

\[
\hat{U}^{ee} = \frac{1}{2} \sum_{\sigma \sigma'} \int d^3r \int d^3r' \; \hat{\Psi}_{\sigma}^\dagger (r) \hat{\Psi}_{\sigma'}^\dagger (r') \frac{1}{|r - r'|} \hat{\Psi}_{\sigma'} (r') \hat{\Psi}_{\sigma} (r) \tag{2.3}
\]

\[
\hat{V}^e = \sum_\sigma \int d^3r \; \hat{\Psi}_{\sigma}^\dagger (r) \hat{v}_{\text{ext}} (r) \hat{\Psi}_{\sigma} (r), \tag{2.4}
\]

the ionic kinetic energy and the ion-ion interaction

\[
\hat{T}^i = \sum_\alpha \int d^3R \; \hat{\Phi}_{\alpha}^\dagger (R) \left( -\frac{\nabla^2}{2M_\alpha} \right) \hat{\Phi}_{\alpha} (R) \tag{2.5}
\]

\[
\hat{U}^{ii} = \frac{1}{2} \sum_{\alpha, \alpha'} \int d^3R \int d^3R' \; \hat{\Phi}_{\alpha}^\dagger (R) \hat{\Phi}_{\alpha'}^\dagger (R') \frac{Z_\alpha Z_{\alpha'}}{|R - R'|} \hat{\Phi}_{\alpha'} (R') \hat{\Phi}_{\alpha} (R), \tag{2.6}
\]

the electron-ion interaction

\[
\hat{U}^{ei} = -\sum_\sigma \sum_\alpha \int d^3r \int d^3R \; \hat{\Psi}_{\sigma}^\dagger (r) \hat{\Phi}_{\alpha}^\dagger (R) \frac{Z_\alpha}{|r - R|} \hat{\Phi}_{\alpha} (R) \hat{\Psi}_{\sigma} (r) \tag{2.7}
\]

and an external pair potential

\[
\hat{\Delta} = -\int d^3r \int d^3r' \left( \Delta_{\text{ext}}^*(r, r') \hat{\Psi}_\uparrow (r) \hat{\Psi}_\downarrow (r') + h.c. \right). \tag{2.8}
\]

\(^1\)atomic units are used throughout.
Here $\sigma$ denotes the electronic spin while $\alpha$ counts the various nuclear species present in the solid. The last term is added as formal device to break the gauge invariance of the Hamiltonian. Since, at this level, the ions are taken into account explicitly, the lattice potential is not treated as an external field. Thus, both $v_{\text{ext}}^e(r)$ and $\Delta_{\text{ext}}(r, r')$ are set to zero at the end of the calculation, if no other external sources like external electric fields or external pair potentials induced by proximity effect are considered.

### 2.2 Hohenberg-Kohn theorem

The density-functional theory (DFT) for the coupled electron-ion system will be based on the following “densities”:

- the electronic density

\[
n(r) = \sum_{\sigma} \langle \hat{\Psi}_{\sigma}^\dagger(r) \hat{\Psi}_{\sigma}(r) \rangle \tag{2.9}
\]

- the anomalous density

\[
\chi(r, r') = \langle \hat{\Psi}_{\uparrow}^\dagger(r) \hat{\Psi}_{\uparrow}(r') \rangle \tag{2.10}
\]

which is the order parameter of the superconducting state as well as its complex conjugate

\[
\chi^*(r, r') = \langle \hat{\Psi}_{\downarrow}^\dagger(r') \hat{\Psi}_{\downarrow}(r) \rangle \tag{2.11}
\]

and

- the diagonal part of the two-particle density matrix of the ions

\[
\Gamma_{\alpha, \alpha'}(R, R') = \langle \hat{\Phi}_{\alpha}^\dagger(R) \hat{\Phi}_{\alpha'}^\dagger(R') \hat{\Phi}_{\alpha'}(R') \hat{\Phi}_{\alpha}(R) \rangle \tag{2.12}
\]

\[
= \langle \hat{N}_\alpha(R) \hat{N}_{\alpha'}(R') \rangle + \zeta_\alpha \delta_{\alpha, \alpha'} \delta(R - R') N_\alpha(R) \tag{2.13}
\]

where $\zeta_\alpha = +1$ for Bosonic and $\zeta_\alpha = -1$ for Fermionic Nuclei. It immediately follows that

\[
\int d^3 R \Gamma_{\alpha, \alpha'}(R, R') = (N_\alpha + \zeta_\alpha \delta_{\alpha, \alpha'}) N_{\alpha'}(R'), \tag{2.14}
\]

\[
\int d^3 R' \Gamma_{\alpha, \alpha'}(R, R') = (N_{\alpha'} + \zeta_{\alpha'} \delta_{\alpha, \alpha'}) N_\alpha(R) \tag{2.15}
\]

and

\[
\Gamma_{\alpha, \alpha'}(R, R') = \Gamma_{\alpha', \alpha}(R', R) \tag{2.16}
\]

where $N_\alpha$ is the number of ions of type $\alpha$ in the integration volume $V$ and $N_\alpha(R)$ is the one-particle density of the ions $\alpha$. The reason for using this diagonal of the two-particle density matrix is that we are interested in the phonons. If one had formulated the theory in terms of the normal ion density, the ionic Kohn-Sham equation would not give rise to realistic phonons. This point will be discussed again in section 2.4 on the transformation to phonon coordinates.
Chapter 2. Basic theorems

The bracket \((\ldots)\) denotes the thermal expectation value:

\[
\langle \hat{A} \rangle = \text{Tr} \left\{ \hat{\rho}_0 \hat{A} \right\} \quad (2.17)
\]

with the grand canonical statistical density operator

\[
\hat{\rho}_0 = \frac{e^{-\beta \hat{H}}}{\text{Tr} \left\{ e^{-\beta \hat{H}} \right\}} \quad (2.18)
\]

The ion-ion interaction \(U_{ii}^\text{ext} \), which is the conjugated potential to \(\Gamma_{\alpha,\alpha'}(\mathbf{R},\mathbf{R}')\), is treated as an “external” potential which couples to the two-particle density matrix \(\Gamma_{\alpha,\alpha'}(\mathbf{R},\mathbf{R}')\). The Hohenberg-Kohn (HK) theorem can then be formulated as follows:

1. there exists a one-to-one mapping of the set of “densities” \(\{n(r), \chi(r, r'), \Gamma_{\alpha,\alpha'}(\mathbf{R},\mathbf{R}')\}\) onto the set of “potentials” \(\{v^e(r) - \mu, \Delta(r, r'), U_{\alpha,\alpha'}(\mathbf{R},\mathbf{R}')\}\),

2. all observables are functionals of these densities, and

3. there exists a variational principle:

\[
\Omega[n_0, \chi_0, \Gamma_0] = \Omega_0 \quad \text{for the equilibrium densities} \quad (2.19)
\]
\[
\Omega[n, \chi, \Gamma] > \Omega_0 \quad \text{for} \quad \{n, \chi, \Gamma\} \neq \{n_0, \chi_0, \Gamma_0\}. \quad (2.20)
\]

where

\[
\Omega[n, \chi, \Gamma] = F[n, \chi, \Gamma] + \int d^3 r n(r)(v^e_{\text{ext}}(r) - \mu)
\]
\[+ \int d^3 r \int d^3 r' (\chi(r, r')\Delta^*_{\text{ext}}(r, r') + h.c.)
\]
\[+ \sum_{\alpha,\alpha'} \int d^3 R \int d^3 R' \Gamma_{\alpha,\alpha'}(\mathbf{R},\mathbf{R}')U_{ii}^\text{ext}(\mathbf{R}, \mathbf{R}'), \quad (2.21)
\]

with the universal functional \(F[n, \chi, \Gamma]\)

\[
F[n, \chi, \Gamma] = (T^e[n, \chi, \Gamma] + U_{ee}[n, \chi, \Gamma])
\]
\[+ T^i[n, \chi, \Gamma] + U_{ei}[n, \chi, \Gamma] - \frac{1}{\beta}S[n, \chi, \Gamma]. \quad (2.22)
\]

The entropy is given by

\[
S[n, \chi, \Gamma] = -\text{Tr} \left\{ \hat{\rho} [n, \chi, \Gamma] \ln(\hat{\rho}[n, \chi, \Gamma]) \right\}. \quad (2.24)
\]

The proof of the theorem follows closely the one of ordinary DFT at finite temperatures [22]. The grand-canonical potential for a given set of potentials is given by:

\[
\Omega_0 = \text{Tr} \left\{ \hat{\rho}_0 \left( \hat{H} + \frac{1}{\beta} \ln(\hat{\rho}_0) \right) \right\} \quad (2.25)
\]
For arbitrary statistical density operators $\hat{\rho}'$ one can define the functional

$$\Omega[\hat{\rho}'] := \text{Tr} \left\{ \hat{\rho}' \left( H + \frac{1}{\beta} \ln(\hat{\rho}') \right) \right\}.$$  

(2.26)

This functional is minimized by the grand canonical statistical operator $\hat{\rho}_0$, i.e.

$$\Omega[\hat{\rho}'] > \Omega[\hat{\rho}_0]$$  

(2.27)

for statistical density operators different from the equilibrium operator $\hat{\rho}_0$. For a given set of potentials the densities can be uniquely defined by solving the Schrödinger equation and evaluating the corresponding expectation values. The other direction can be shown as follows: Let $\{n, \chi, \Gamma\}$ be the equilibrium densities obtained from the set of potentials $\{v_{\text{ext}}^e - \mu, \Delta_{\text{ext}}, U^{ii}\}$. Assume that another set of potentials $\{v_{\text{ext}}^e' - \mu', \Delta_{\text{ext}}', U^{ii'}\}$ exists which results in the same equilibrium densities. The grand-canonical potential of the unprimed system can, by addition and subtraction of the primed potentials, be expressed as:

$$\Omega[\hat{\rho}_0] = \text{Tr} \left\{ \hat{\rho}_0 \left( H + \frac{1}{\beta} \ln(\hat{\rho}_0) \right) \right\}$$

$$= \text{Tr} \left\{ \hat{\rho}_0 \left( H' + \frac{1}{\beta} \ln(\hat{\rho}_0) \right) \right\} + \text{Tr} \left\{ \hat{\rho}_0 \left( H - H' \right) \right\}$$

$$= \Omega'[\hat{\rho}_0] + \Delta \Omega$$  

(2.28)

with

$$\Delta \Omega = \int d^3 r n(r) (v_{\text{ext}}^e(r) - \mu - v_{\text{ext}}^e'(r) - \mu')$$

$$- \int d^3 r \int d^3 r' \left[ \chi(r, r') (\Delta_{\text{ext}}^*(r, r') - \Delta_{\text{ext}}'^*(r, r')) + h.c. \right]$$

$$+ \sum_{a, a'} \int d^3 R \int d^3 R' \Gamma_{a, a'} (R, R') (U_{a, a'}^{ii'}(R, R') - U_{a, a'}^{ii}(R, R')).$$  

(2.29)

Since $\hat{\rho}_0$ does not minimize the primed system, one can write

$$\Omega[\hat{\rho}_0] > \Omega'[\hat{\rho}_0'] + \Delta \Omega$$  

(2.30)

where $\hat{\rho}_0'$ is the statistical density operator of the primed system:

$$\hat{\rho}_0' = \frac{e^{-\beta \hat{H}'}}{\text{Tr} \left\{ e^{-\beta \hat{H}'} \right\}}.$$  

(2.31)

Starting with the primed system the reversed can be obtained in the same way:

$$\Omega'[\hat{\rho}_0] > \Omega[\hat{\rho}_0] - \Delta \Omega.$$  

(2.32)

Adding these equations one gets the contradiction

$$\Omega[\hat{\rho}_0] + \Omega'[\hat{\rho}_0'] > \Omega[\hat{\rho}_0] + \Omega'[\hat{\rho}_0']$$  

(2.33)
falsifying the assumption that different sets of potentials can result in the same set of densities. This establishes the one-to-one mapping. Since the statistical operator was completely determined by the potentials, it can be seen that all observables, which are expectation values of the corresponding operators with respect to this statistical operator, are functionals of the set of densities. This holds in particular for the grand canonical potential. The variational scheme is then evident. The existence of the universal functional $F$ follows immediately by separating the terms containing the external fields.

The proof of the variational scheme requires some more caution. The use of the two-particle density matrix for the ions causes a representability problem. There exist functions $\Gamma(R, R')$ which cannot be obtained from any many-body wave function. Minimizing freely over those functions might result in a minimum lower than the physical one. This problem can be solved with the constrained search formalism [23, 24, 25]. The equilibrium condition is:

$$\Omega_0 = \min_{\rho} \Omega[\rho]. \quad (2.34)$$

This minimization can be split into a constrained minimization over all statistical operators yielding a given set of densities and an subsequent minimization over the densities.

$$\Omega_0 = \min_{\{n, \chi, \Gamma\}} \left( \min_{\rho \rightarrow \{n, \chi, \Gamma\}} \Omega[\rho] \right). \quad (2.35)$$

The functional defined in this way fulfills the variational principle. It should be noted that the constrained search formulation solves the $n$-representability problem, but similar to other extensions of DFT we have to assume the non-interacting $\nu$-representability.

### 2.3 Kohn-Sham system

The HK theorem, which is true for each fixed electron-electron interaction $U^{ee}$ and each fixed electron-ion interaction $U^{ei}$, can be used to construct an auxiliary “non-interacting” system, the Kohn-Sham (KS) system, with effective external potentials leading to the same set of densities as the original interacting system. The word “non-interacting” has to be interpreted in different ways for the ions and the electrons. In the case of the ions, the KS system will consist of ions, interacting via an effective two-particle interaction, but not interacting with the electrons. The KS system of the electrons will be the usual KS system, i.e. electrons not interacting among themselves but interacting with the ions.

The KS system can be obtained by rewriting the free-energy functional $F$

\begin{align*}
F[n, \chi, \Gamma] &= (T^{e}[n, \chi, \Gamma] + U^{ee}[n, \chi, \Gamma]) \\
&+ T^{i}[n, \chi, \Gamma] + U^{ei}[n, \chi, \Gamma] - \frac{1}{\beta} S[n, \chi, \Gamma] \quad (2.36)
\end{align*}
2.3. Kohn-Sham system

in terms of expectation values of a non-interacting system:

\[
F[n, \chi, \Gamma] = T^e_s[n, \chi, \Gamma] + T^i_s[n, \chi, \Gamma] + E^e_H[n] + E^e_i[n, \Gamma] - \frac{1}{\beta} S_s[n, \chi, \Gamma] + F_{xc}[n, \chi, \Gamma]
\]

where the exchange-correlation term is formally defined as

\[
F_{xc}[n, \chi, \Gamma] = \left[ (T^e[n, \chi, \Gamma] - T^e_s[n, \chi, \Gamma]) + (U^e[n, \chi, \Gamma] - E^e_H[n]) \right] + \left[ (T^i[n, \chi, \Gamma] - T^i_s[n, \chi, \Gamma]) + (U^i[n, \chi, \Gamma] - E^i_H[n, \Gamma]) \right] - \frac{1}{\beta}(S[n, \chi, \Gamma] - S_s[n, \chi, \Gamma]).
\]

The Hartree terms are defined as:

\[
E^e_H[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(r)n(r')}{|r - r'|}
\]

\[
E^e_i[n, \Gamma] = -\frac{1}{2m} \sum_{\alpha, \alpha'} \int d^3r \int d^3R \int d^3R' n(r) \Gamma_{\alpha, \alpha'}(R, R') \times
\]

\[
\left( \frac{Z_{\alpha}}{N_{\alpha'} + \zeta_{\alpha'} \delta_{\alpha, \alpha'}} \frac{1}{|r - R|} + \frac{Z_{\alpha'}}{N_{\alpha} + \zeta_{\alpha} \delta_{\alpha, \alpha'}} \frac{1}{|r - R'|} \right)
\]

where \( m \) is the number of different types of ions. The ionic KS Hamiltonian then reads:

\[
\hat{H}_{KS}^i = \hat{T}^i + \hat{U}^{iii} + \sum_{\alpha, \alpha'} \int d^3R \int d^3R' \hat{\Gamma}_{\alpha, \alpha'}(R, R') (V_{H, \alpha, \alpha'}^{ei}[n, \Gamma](R, R') + V_{c, \alpha, \alpha'}^{ei}[n, \chi, \Gamma](R, R'))
\]

with

\[
V_{H, \alpha, \alpha'}^{ei}[n, \Gamma](R, R') = \frac{\delta E^e_H[n, \Gamma]}{\delta \Gamma_{\alpha, \alpha'}(R, R')}
\]

\[
= \frac{1}{2m} \int d^3r \left( \frac{Z_{\alpha}}{N_{\alpha'} + \zeta_{\alpha'} \delta_{\alpha, \alpha'}} \frac{n(r)}{|r - R|} + \frac{Z_{\alpha'}}{N_{\alpha} + \zeta_{\alpha} \delta_{\alpha, \alpha'}} \frac{n(r)}{|r - R'|} \right)
\]

\[
V_{c, \alpha, \alpha'}^{ei}[n, \chi, \Gamma](R, R') = \frac{\delta F_{xc}[n, \chi, \Gamma]}{\delta \Gamma_{\alpha, \alpha'}(R, R')}
\]

whereas the electronic KS Hamiltonian is given by:

\[
\hat{H}_{KS}^e = \hat{T}^e + \int d^3r n(r) \left( v^e_{\text{ext}}(r) - \mu \right)
\]

\[
+ \int d^3r n(r) \left( v^e_H[n](r) + v^e_H[n, \Gamma](r) + v_{xc}[n, \chi, \Gamma](r) \right)
\]

\[
- \int d^3r \int d^3r' \left[ \chi(r, r') \left( \Delta^e_{\text{ext}}(r, r') + \Delta^e_{xc}[n, \chi, \Gamma](r, r') \right) + h.c. \right]
\]
with
\[ v_{ii}[n](r) = \frac{\delta E_{ii}^n}{\delta n(r)} = \int d^3 r' \frac{n(r')}{|r - r'|} \]  
(2.46)
\[ v_{ii}^{ei}[n, \Gamma](r) = \frac{\delta E_{ii}^{ei}[n, \Gamma]}{\delta n(r)} = - \sum Z_\alpha \int d^3 R \frac{N_\alpha(R)}{|r - R|} \]  
(2.47)
\[ v_{xc}[n, \chi, \Gamma](r) = \frac{\delta F_{xc}[n, \chi, \Gamma]}{\delta n(r)} \]  
(2.48)
\[ \Delta_{xc}[n, \chi, \Gamma](r, r') = \frac{\delta F_{xc}[n, \chi, \Gamma]}{\delta \chi^*(r, r')} \]  
(2.49)

### 2.4 KS equation for the ions – KS phonons

The ionic KS equation reads:
\[
\left\{ \sum_\alpha \int d^3 \hat{R}_\alpha(R) \left(-\frac{\nabla^2}{2M_\alpha}\right) \hat{\phi}_\alpha(R) \right.
+ \sum_{\alpha, \alpha'} \int d^3 R \int d^3 R' \tilde{V}_{\alpha, \alpha'}(R, R') V_{s\alpha, \alpha'}^i (R, R') \phi_{\alpha} \phi_{\alpha'} \bigg| \phi_n \bigg) = E_n \phi_n
\]  
(2.50)

or in first quantization
\[
\left( \sum_{i, \alpha} \left(-\frac{\nabla^2}{2M_\alpha}\right) + \sum_{(\alpha, i) \neq (\alpha', j)} V_{s\alpha, \alpha'}^i (R_{\alpha, i}, R_{\alpha', j}) \right) \phi_n (R) = E_n \phi_n (R)
\]  
(2.51)

where the roman labels at the ion-coordinates indicate the individual ions and the type of an ion is given by the greek label. The set of all ionic coordinates \( \{R_{\alpha, i}\} \). The effective two-particle potential is:
\[
V_{s\alpha, \alpha'}^i (R_{\alpha, i}, R_{\alpha', j}) = \frac{1}{2} \frac{Z_\alpha Z_{\alpha'}}{|R - R'|} + V_{s\alpha, \alpha'}^{ei} (R, R') + V_{c\alpha, \alpha'}^{ei} (R, R').
\]  
(2.52)

In a solid the ions are well localized around their equilibrium positions. These are defined by the minimum of the many-body potential acting on the ions
\[
\nabla V(R) \bigg|_{R=R^0} = 0
\]  
(2.53)

where
\[
V(R) = \frac{1}{2} \sum_{(\alpha, i) \neq (\alpha', j)} V_{s\alpha, \alpha'}^{ii} (R_{\alpha, i}, R_{\alpha', j}).
\]  
(2.54)

This potential \( V \) can formally be expanded around the equilibrium positions:
\[
V(R) = V(R^0) + \sum_\alpha \sum_i \sum_\mu \left( \nabla_{\alpha, i}^{\mu} \right) \left( \frac{\partial^\mu}{\partial \alpha, i} V(R) \bigg|_{R=R^0} \right)
\]  
(2.55)
\[ 2.4. \text{KS equation for the ions – KS phonons} \]

\[ + \frac{1}{2!} \sum_{\alpha,\alpha'} \sum_{i,j} \sum_{\mu,\nu} U_{\alpha,i}^\mu U_{\alpha',j}^{\mu'} \left( \frac{\partial_{\alpha,i}^\mu \partial_{\alpha',j}^{\mu'}}{2M_{\alpha}} \right) = \hat{H}_{ph} \]

\[ + \frac{1}{3!} \sum_{\alpha,\alpha',\alpha''} \sum_{i,j,k} \sum_{\mu,\nu,\lambda} U_{\alpha,i}^\mu U_{\alpha',j}^{\mu'} U_{\alpha'',k}^{\nu} \left( \frac{\partial_{\alpha,i}^\mu \partial_{\alpha',j}^{\mu'} \partial_{\alpha'',k}^{\nu}}{2M_{\alpha}} \right) + O(U)^4 \]

where \( \mu \) and \( \nu \) label the three spatial coordinates \( x, y \) and \( z \). Assuming that the terms of third and higher order are small and can be treated by perturbation theory later on, we consider the Hamiltonian:

\[ \hat{H}_{ph} = \sum_{\alpha} \sum_i \sum_{\mu} \left( \frac{(\hat{P}_{\alpha,i}^\mu)^2}{2M_{\alpha}} \right) + \frac{1}{2} \sum_{\alpha,\alpha'} \sum_{i,j} \sum_{\mu,\nu} \left( \hat{U}_{\alpha,i}^\mu \hat{A}_{\alpha,i;\alpha',j}^{\mu'} \hat{U}_{\alpha',j}^{\mu'} \right) \cdot (2.56) \]

Defining the Fourier transforms:

\[ \hat{U}_{(\alpha,\mu),q} := \frac{1}{\sqrt{N}} \sum_{R_{\alpha,i} \in V} e^{-iqR_{\alpha,i}^\mu} \hat{U}_{\alpha,i}^\mu \quad (2.57) \]

\[ \hat{P}_{(\alpha,\mu),q} := \frac{i}{\sqrt{N}} \sum_{R_{\alpha,i} \in V} e^{iqR_{\alpha,i}^\mu} \hat{P}_{\alpha,i}^\mu \quad (2.58) \]

where \( N \) is the number of elementary cells in the volume \( V \), the Hamiltonian can be written as

\[ \hat{H}_{ph} = \sum_{(\alpha,\mu)} \sum_q \left( \frac{\hat{P}_{(\alpha,\mu),q}^\dagger \hat{P}_{(\alpha,\mu),q}}{2M_{\alpha}} \right) + \frac{1}{2} \sum_{(\alpha,\mu)} \sum_q \sum_{(\alpha',\mu')} \hat{U}_{(\alpha,\mu),q} \Lambda_{(\alpha,\mu),(\alpha',\mu'),q} \hat{U}_{(\alpha',\mu'),q} \quad (2.59) \]

where

\[ \Lambda_{(\alpha,\mu),(\alpha',\mu'),q} := \sum_i e^{iq(R_{\alpha,\mu} - R_{\alpha',\mu'})} A_{\alpha,\beta;\alpha',\beta'}^{\mu,\mu'} \quad (2.60) \]

\( \Lambda \) is a 3m dimensional matrix, where \( m \) is the the total number of atoms in a elementary cell. The eigenvectors of \( \Lambda \), denoted by \( \xi_{\lambda,q}^{(\alpha,\mu)} \), are the eigenmodes of the system and form the polarization vectors\(^2\):

\[ \sum_{(\alpha',\mu')} \Lambda_{(\alpha,\mu),(\alpha',\mu'),q} \xi_{\lambda,q}^{(\alpha',\mu')} = M_{\alpha} \Omega_{\lambda,q}^2 \xi_{\lambda,q}^{(\alpha,\mu)} \quad (2.61) \]

\(^2\)If an ordinary KS scheme for the ions was used, i.e. describing the ions by their density, the effective potential \( V(R) \) would be the sum of one-particle potentials, and thus independent of \( R_i - R_j \). In this case the ionic KS equation would not lead to realistic phonons with a proper dispersion relation. Only Einstein phonons could be present in this KS system. This is also clear from the fact that a simple system of non-interacting particles does not show collective modes.
\( \lambda \) labels the different phonon branches, including the acoustical and the optical modes. These eigenvectors can be used to define a new set of collective coordinates

\[
\sqrt{M_\alpha} U_{(\alpha, \mu);q} = \sum_\lambda \xi^{(\alpha, \mu)}_{\lambda,q} \dot{Q}_\lambda,q
\]  

(2.62)

\[
\frac{\dot{P}_{(\alpha, \mu);q}}{\sqrt{M_\alpha}} = \sum_\lambda \xi^{(\alpha, \mu)}_{\lambda,q} \dot{\Pi}_\lambda,q
\]  

(2.63)

leading to:

\[
\dot{H}_{ph} = \sum_{\lambda,q} \left[ \frac{1}{2} \Pi_{\lambda,q}^t \Pi_{\lambda,q} + \frac{1}{2} \Omega_{\lambda,q}^2 \dot{Q}_\lambda,q^t \dot{Q}_\lambda,q \right].
\]  

(2.64)

This Hamiltonian can be diagonalized by introducing

\[
\hat{b}_{\lambda,q} := \frac{1}{\sqrt{2 \Omega_{\lambda,q}}} \left( \Omega_{\lambda,q} \dot{Q}_{\lambda,q} + i \dot{\Pi}_{\lambda,q} \right)
\]  

(2.65)

\[
\hat{b}_{\lambda,q}^\dagger := \frac{1}{\sqrt{2 \Omega_{\lambda,q}}} \left( \Omega_{\lambda,q} \dot{Q}_{\lambda,q}^t - i \dot{\Pi}_{\lambda,q} \right),
\]  

(2.66)

leading to

\[
\dot{H}_{ph} = \sum_{\lambda,q} \Omega_{\lambda,q} \left( \hat{b}_{\lambda,q}^\dagger \hat{b}_{\lambda,q} + \frac{1}{2} \right).
\]  

(2.67)

The small deviations from the equilibrium positions can then be expressed by:

\[
\hat{U}_\alpha,i^\mu = \frac{1}{\sqrt{2NM_\alpha}} \sum_{\lambda,q} e^{i q R_{\alpha,i}^0} \xi^{(\alpha, \mu)}_{\lambda,q} \hat{\Phi}_{\lambda,q}
\]  

(2.68)

with

\[
\hat{\Phi}_{\lambda,q} = \left( \hat{b}_{\lambda,q} + \hat{b}_{\lambda,-q}^\dagger \right).
\]  

(2.69)

Anharmonic terms can now be added perturbatively. The first term would be of the form:

\[
\dot{H}_{ph-ph} = \sum_{\lambda,q} \sum_{\lambda',q'} \sum_{\lambda'',q''} \Gamma_{\lambda,q;\lambda',q';\lambda'',q''} \hat{\Phi}_{\lambda,q} \hat{\Phi}_{\lambda',q'} \hat{\Phi}_{\lambda'',q''}.
\]  

(2.70)

Since, up to now, no reliable approximation for the ionic correlation potential is available, we will approximate the many-body potential arising from \( V_{ei}^H + V_{ei}^c \) by the Born-Oppenheimer potential. In this case, the phonon frequencies and electron-phonon coupling constants, to be used in the following, can be taken from Born-Oppenheimer calculations, like the linear-response calculations performed by Savrasov [26, 27] or Yu and Krakauer [28]. In principle, the electron-ion correlation potential depends of course also on the superconducting order parameter. There are also experiments which measure the dependency of the phonon frequencies and line widths on the temperature and exhibit a anomaly at the superconducting transition temperature [29, 30, 31]. In general, these effects are rather small and will henceforth be neglected. In principle, however, the formalism developed here can describe these effects if one finds an appropriate approximation for the electron-ion correlation energy.
2.5 KS-Bogoliubov-de Gennes equations

The Hamiltonian of the non-interacting electron system is:
\[
H_s = \sum_{\sigma} \int d^3r \hat{H}_{\sigma}^I(r) \left( -\frac{\nabla^2}{2} + v_s(r) - \mu \right) \hat{\Psi}_{\sigma}(r) - \int d^3r \int d^3r' \left( \Delta_s^*(r, r') \hat{\Psi}^\dagger_{\uparrow}(r') \hat{\Psi}_{\downarrow}(r) + \Delta_s(r, r') \hat{\Psi}^\dagger_{\downarrow}(r') \hat{\Psi}_{\uparrow}(r) \right). \tag{2.71}
\]

This Hamiltonian can be diagonalized with the Bogoliubov transformation \cite{32}:
\[
\hat{\Psi}_{\sigma}(r) = \sum_{i} \left( u_i(r) \hat{\gamma}_{i\sigma} - \text{sgn}(\sigma) v_i^*(r) \hat{\gamma}_{i-\sigma}^\dagger \right) \tag{2.72}
\]
where the \( u_i(r) \) and \( v_i(r) \) are the solutions of the Kohn-Sham-Bogoliubov-de Gennes (KS-BdG) equations
\[
\left( -\frac{\nabla^2}{2} + v_s(r) - \mu \right) u_i(r) + \int d^3r' \Delta_s(r, r') v_i(r') = E_i u_i(r) \tag{2.73}
\]
\[- \left( -\frac{\nabla^2}{2} + v_s(r) - \mu \right) v_i(r) + \int d^3r' \Delta_s^*(r, r') u_i(r') = E_i v_i(r) \tag{2.74}
\]
and \( \hat{\gamma}_{i}^\dagger \) and \( \hat{\gamma}_{i} \) are Fermionic creation and annihilation operators. In the non-interacting system the densities (2.9) and (2.10) can be expressed in terms of the particle and hole amplitudes \( u_i(r) \) and \( v_i(r) \):
\[
n(r) = 2 \sum_i \left( |u_i(r)|^2 f_\beta(E_i) + |v_i(r)|^2 f_\beta(-E_i) \right) \tag{2.75}
\]
\[
\chi(r, r') = \sum_i (u_i(r)v_i^*(r')f_\beta(-E_i) - v_i^*(r)u_i(r')f_\beta(E_i)) \tag{2.76}
\]
where \( f_\beta(E) \) is the Fermi distribution function. The effective potentials are:
\[
v_s(r) = v_s^e(r) + v_{\text{ext}}^e[n](r) + v_{\text{H}}^e[n, \Gamma](r) + v_{\text{xc}}[n, \chi, \Gamma](r) \tag{2.77}
\]
\[
\Delta_s(r, r') = \Delta_{\text{ext}}(r, r') + \Delta_{\text{xc}}[n, \chi, \Gamma](r, r') \tag{2.78}
\]
with
\[
v_{\text{xc}}[n, \chi, \Gamma](r) := \frac{\delta F_{\text{xc}}[n, \chi, \Gamma]}{\delta n(r)}, \tag{2.79}
\]
\[
\Delta_{\text{xc}}[n, \chi, \Gamma](r, r') := -\frac{\delta^2 F_{\text{xc}}[n, \chi, \Gamma]}{\delta \chi_{r'}^r}. \tag{2.80}
\]
Formally these equations equal exactly those of the previous DFT formulation for superconducting systems \cite{15, 18}. The differences are that in this case the lattice potential enters as the zeroth order of the electron-ion Hartree term, and that the \( \text{xc} \) terms depend on the ionic density matrix and thus on the phonons.
2.6 Decoupling approximation – KS gap equation

A direct solution of the KS-BdG equations [33] is faced with the problem that one needs extremely high accuracy to resolve the energy scale of the superconducting gap, which usually is about three orders of magnitude smaller than typical electronic energies of the normal phase, while, at the same time, one has to cover the whole energy range of the electronic band structure. Therefore it appears desirable to decouple these energy scales by deriving separate equations, one for each energy scale.

To achieve this, we expand the solutions of the KS-BdG equations and the pair potential in terms of the KS orbitals

\[
\begin{align*}
    u_i(r) &= \sum_k u_{i,k} \varphi_k(r) \\
    v_i(r) &= \sum_k v_{i,k} \varphi_k(r) \\
    \Delta_s(r, r') &= \sum_{kk'} \Delta_{k,k'} \varphi_k(r) \varphi_{k'}^*(r')
\end{align*}
\]

which are solutions of the auxiliary KS equation

\[
\left( -\frac{\nabla^2}{2} + v_s[n, \chi, \Gamma](r) - \mu \right) \varphi_k(r) = \varepsilon_k \varphi_k(r). \quad (2.84)
\]

For vanishing external potential, i.e. \( v_{ext}^e(r) = 0 \), which is the case of interest, the KS orbitals are Bloch orbitals. In the spin-independent case we can use their behavior with respect to time-reversal \( \hat{T} \):

\[
\varphi_k^*(r) = \hat{T} \varphi_k(r) := \varphi_k(r). \quad (2.85)
\]

Inserting this into the KS-BdG equations (2.73),(2.74) and using the orthonormality of the Bloch orbitals, we obtain

\[
\begin{align*}
    (\varepsilon_q - \mu) u_{i,q} + \sum_k \Delta_{q,k} v_{i,k} &= E_i u_{i,q} \\
    \sum_k \Delta_{q,k}^* u_{i,k} - (\varepsilon_q - \mu) v_{i,q} &= E_i v_{i,q}
\end{align*}
\]

This can be written as a matrix equation

\[
\sum_k \hat{H}_{q,k} \Psi_{i,k} = E_i \Psi_{i,q} \quad (2.88)
\]

with

\[
\Psi_{i,q} = \begin{pmatrix} u_{i,q} \\ v_{i,q} \end{pmatrix}, \quad \hat{H}_{q,k} = \begin{pmatrix} (\varepsilon_k - \mu) \delta_{q,k} & \Delta_{q,k} \\ \Delta_{q,k}^* & -(\varepsilon_k - \mu) \delta_{q,k} \end{pmatrix}. \quad (2.89)
\]

\[3\] to keep the notation readable the subscript “s” which indicates the KS potential is dropped for the matrix elements of the pair potential.
The matrix elements of the pair potential are given by:

$$\Delta_{k,k'} = \Delta_{\text{ext}} k,k' + \Delta_{\text{xc}} k,k'. \tag{2.90}$$

As it is shown in appendix A, the matrix elements of the pair potential are diagonal with respect to all symmetry related quantum numbers. The decoupling approximation is to neglect elements which are off-diagonal with respect to the principal quantum number, i.e.

$$\Delta_{k,k'} = \delta_{k,k'} \Delta_k. \tag{2.91}$$

This approximation is motivated by the consideration that the important matrix elements will be those between states of equal or nearly equal energy. As can be seen later in Eq. (2.103) this approximation is physically motivated by the assumption that the Cooper pairs are formed by electrons in time-reversed states. This approximation might break down if two bands of the same symmetry cross each other in the vicinity of the Fermi surface.

With this approximation the $2n \times 2n$ matrix $H$ factorizes into $n \times 2 \times 2$ matrices

$$\begin{pmatrix} (\varepsilon_k - \mu) & \Delta_k \\ \Delta_k^* & -(\varepsilon_k - \mu) \end{pmatrix}. \tag{2.92}$$

The eigenvalues are$^4$:

$$E_k^\pm = \pm R_k \tag{2.93}$$

$$R_k = + \sqrt{(\varepsilon_k - \mu)^2 + \Delta_k \Delta_k^*} \tag{2.94}$$

$$= + \sqrt{(\varepsilon_k - \mu)^2 + |\Delta_k|^2} \tag{2.95}$$

and the corresponding eigenvectors are given by:

$$\Psi_{i,k} = \delta_{i,k} \begin{pmatrix} u_k \\ v_k \end{pmatrix} \tag{2.96}$$

with

$$u_k = \frac{1}{\sqrt{2}} \text{sgn}(E_k) e^{i\delta_k} \left[ 1 + \frac{\varepsilon_k - \mu}{E_k} \right]^{\frac{1}{2}} \tag{2.97}$$

$$v_k = \frac{1}{\sqrt{2}} \left[ 1 - \frac{\varepsilon_k - \mu}{E_k} \right]^{\frac{1}{2}} \tag{2.98}$$

where

$$e^{i\delta_k} = \frac{\Delta_k}{|\Delta_k|} \tag{2.99}$$

is the phase of the order parameter. The particle and hole amplitudes read:

$$u_k(\mathbf{r}) = u_k \varphi_k(\mathbf{r}) \tag{2.100}$$

$$v_k(\mathbf{r}) = v_k \varphi_k(\mathbf{r}). \tag{2.101}$$

$^4$From $\Delta_a(\mathbf{r}, \mathbf{r'}) = \Delta_a(\mathbf{r'}, \mathbf{r})$ follows $\Delta_k = \Delta_k$, see Appendix A.
It should be noted that this form, often used as Ansatz for the particle and hole amplitudes, can be justified in this way as a consequence of the decoupling approximation.

Inserting this in Eqs. (2.75) and (2.76), the density and the anomalous density can be written as:

\[ n(r) = \sum_k \left( 1 - \frac{\varepsilon_k - \mu}{R_k} \tanh\left( \frac{\beta}{2} R_k \right) \right) |\varphi_k(r)|^2 \]  

(2.102)

\[ \chi(r, r') = \frac{1}{2} \sum_k \frac{\Delta_k}{R_k} \tanh\left( \frac{\beta}{2} R_k \right) \varphi_k(r) \varphi_k^*(r') \]  

(2.103)

The pair potential \( \Delta_k \) is then calculated self-consistently by inserting these densities into eq. (2.78) and evaluating

\[ \Delta_k = \int d^3r \int d^3r' \varphi_k^*(r) \Delta_k(r, r') \varphi_k(r') \]  

(2.104)

As will be seen later, the approximation for the exchange-correlation pair potential we will derive will not be given as an explicit functional of the densities, but will be a functional of the chemical potential \( \mu \) and the effective pair potential \( \Delta_k \) itself. Thus one obtains the equation

\[ \Delta_k = \Delta_{\text{ext}} k + \Delta_{\text{xc}} k[\mu, \Delta_k] \]  

(2.105)

which represents the generalized gap equation.

In this way the problem of solving the KS-BdG equations reduces to the problem of solving this gap equation self-consistently with the KS equation

\[ \left( -\nabla^2 + v_s[n, \chi, \Gamma] - \mu \right) \varphi_k(r) = \varepsilon_k \varphi_k(r). \]  

(2.106)

The complete self-consistency cycle is shown in figure 2.1. It has to be noted that the chemical potential \( \mu \) has to be adjusted in every iteration, such that the density \( n(r) \) integrates to the correct particle number \( N \). Also the KS-orbitals \( \varphi_k(r) \), used as basis functions in the expansion of the pair potential and the interactions, change in each iteration, since they are obtained from the KS equation containing the exchange-correlation potential \( v_{\text{xc}}[n, \chi, \Gamma](r) \) which, in principle, depends on the superconducting order parameter.

In the vicinity of the transition temperature, the gap equation can be linearized in \( \Delta_k \), leading to:

\[ \Delta_k = \Delta_{\text{ext}} k - \frac{1}{2} \sum_{k'} f_{\text{xc}}(k; k') \frac{\tanh\left( \frac{\beta}{2} (\varepsilon_{k'} - \mu) \right)}{\varepsilon_{k'} - \mu} \Delta_{k'} \]  

(2.107)

with

\[ f_{\text{xc}}(k; k') := -\left. \frac{\delta \Delta_{\text{xc}} k}{\delta \chi_{k'}} \right|_{\chi=0} = -2 \frac{\varepsilon_{k'} - \mu}{\tanh\left( \frac{\beta}{2} (\varepsilon_{k'} - \mu) \right)} \left. \left( \delta \Delta_{\text{xc}} k \right)_{\Delta=0} \right|_{\Delta=0}. \]  

(2.108)
2.6. Decoupling approximation – KS gap equation

Start approximation:
\[ v_s(r) = v_s[n](r), \Delta_s(r, r') \equiv 0 \]

solve KS equation (2.106) for the \( \varphi_k(r) \)

Decoupling approximation:
\[ u_k(r) = u_k \varphi_k(r) \]
\[ v_k(r) = v_k \varphi_k(r) \]

solve gap equation (2.105) for \( \Delta_k \)

calculate densities \( n \) and \( \chi \)

calculate potentials
\[ v_s[n, \chi, \Gamma](r) \text{ and } \Delta_s[n, \chi, \Gamma](r, r') \]

self-consistency?

no

output  

yes

Figure 2.1: Schematic flow chart for the iteration in the decoupling approximation

This linearized gap equation is of the same structure as the BCS gap equation. The kernel \( f_{xc}(k; k') \) replaces the model interaction of the BCS theory and thus forms an effective interaction which is independent of the pair potential and the anomalous density and which can give some information about the mechanism of superconductivity. It is worth noting that the full gap equation (2.105) cannot be brought into this form with an \( \Delta_k \)-independent kernel.

\[ ^5 \text{In the first cycle an initial, non-zero pair potential has to be used for solving the gap equation to obtain a non-trivial solution.} \]
2.7 The exact linearized gap equation

The linearized gap equation, presented in last section was based on the decoupling approximation. Near the critical temperature \( T \lesssim T_c \), and only in that regime, it is also possible to derive an exact gap equation, i.e., without recourse to the decoupling approximation. In the following we first derive this exact gap equation in the linear regime and then use it to gain more insight about the decoupling approximation.

Consider a system in the normal state, i.e., \( \chi(\mathbf{r}, \mathbf{r}') \equiv 0 \). When the system is cooled below the transition temperature \( T_c \), the normal state becomes unstable. An infinitesimal external pair potential \( \Delta_{\text{ext}}(\mathbf{r}, \mathbf{r}') \) will drive the system into the superconducting state with a finite order parameter \( \chi(\mathbf{r}, \mathbf{r}') \).

The reaction of a system to a small external perturbation can be described by the linear response formalism. In a superconducting system, the linear response to a set of external perturbations \( \{v_1(\mathbf{r}), \Delta_1(\mathbf{r}, \mathbf{r}')\} \) is given by [34, 35, 18]:

\[
\tilde{n}_1 = \int \tilde{\chi} \tilde{v}_1 \quad (2.109)
\]

where

\[
\tilde{n}_1 = \begin{pmatrix} n_1(\mathbf{r}) \\ \chi_1(\mathbf{r}, \mathbf{r}') \\ \chi_1^*(\mathbf{r}, \mathbf{r}') \end{pmatrix}, \quad \tilde{v}_1 = \begin{pmatrix} v_1(\mathbf{x}) \\ \Delta_1(\mathbf{x}, \mathbf{x}') \\ \Delta_1^*(\mathbf{x}, \mathbf{x}') \end{pmatrix}, \quad (2.110)
\]

\[
\tilde{\chi} = \begin{pmatrix} \chi(\mathbf{r}; \mathbf{x}) & \Lambda^*(\mathbf{r}; \mathbf{x}, \mathbf{x}') & \Lambda(\mathbf{r}; \mathbf{x}, \mathbf{x}') \\ \Gamma(\mathbf{r}, \mathbf{r}'; \mathbf{x}) & \Xi(\mathbf{r}, \mathbf{r}'; \mathbf{x}, \mathbf{x}') & \Xi^*(\mathbf{r}, \mathbf{r}'; \mathbf{x}, \mathbf{x}') \\ \Gamma^*(\mathbf{r}, \mathbf{r}'; \mathbf{x}) & \tilde{\Xi}^*(\mathbf{r}, \mathbf{r}'; \mathbf{x}, \mathbf{x}') & \Xi(\mathbf{r}, \mathbf{r}'; \mathbf{x}, \mathbf{x}') \end{pmatrix}. \quad (2.111)
\]

The integrations extend over the arguments of the perturbations.

The functions defined in Eq. (2.111) are the response functions of the full interacting system in the superconducting state. By applying DFT also to the perturbed system, it was shown [34, 35, 18] that the linear response of the interacting system can be calculated as the response of the non-interacting Kohn-Sham system to an effective perturbation:

\[
\tilde{n}_1 = \int \hat{\chi}_{\text{eff}} \tilde{v}_{1,\text{eff}} \quad (2.112)
\]

with

\[
\tilde{v}_{1,\text{eff}} = \tilde{v}_1 + \int \left( \hat{u} + \hat{f}_{\text{xc}} \right) \tilde{n}_1 \quad (2.113)
\]

where

\[
\hat{u} = \begin{pmatrix} 1/|\mathbf{r} - \mathbf{r}'| & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \hat{f}_{\text{xc}} = \begin{pmatrix} \delta v_{\text{xc}}(\mathbf{r})/\delta n(\mathbf{x}) & \delta v_{\text{xc}}(\mathbf{r}')/\delta n(\mathbf{x}) & \delta v_{\text{xc}}(\mathbf{r})/\delta n(\mathbf{x}) \\ \delta v_{\text{xc}}(\mathbf{r})/\delta \Delta_{\text{xc}}(\mathbf{r}, \mathbf{r}') & \delta v_{\text{xc}}(\mathbf{r}')/\delta \Delta_{\text{xc}}(\mathbf{r}, \mathbf{r}') & \delta v_{\text{xc}}(\mathbf{r})/\delta \Delta_{\text{xc}}(\mathbf{r}, \mathbf{r}') \\ \delta v_{\text{xc}}(\mathbf{r})/\delta \Delta_{\text{xc}}(\mathbf{r}, \mathbf{r}') & \delta v_{\text{xc}}(\mathbf{r}')/\delta \Delta_{\text{xc}}(\mathbf{r}, \mathbf{r}') & \delta v_{\text{xc}}(\mathbf{r})/\delta \Delta_{\text{xc}}(\mathbf{r}, \mathbf{r}') \end{pmatrix}.
\]
The response equations are then:

\[ \tilde{n}_1 = \int \chi_s \left[ \tilde{v}_1 + \int \left( \tilde{u} + \tilde{f}_{xc} \right) \tilde{n}_1 \right]. \]  

(2.114)

In order to find the instability of the normal phase, these response equations have to be considered in the normal (N) state, i.e., for \( \chi \equiv 0 \). It follows from explicit calculations of the response functions, that only the three diagonal response functions remain finite in the normal limit. Furthermore it can be seen from the gauge invariance of the Hamiltonian, that also the off-diagonal elements of \( \tilde{f}_{xc} \) vanish in the normal limit. Hence the response equations decouple into:

\[ n_1(\mathbf{r}) = \int d^3x \chi_s^N(\mathbf{r}, \mathbf{x}) \left[ v_1(\mathbf{x}) + \int d^3y \left( \frac{1}{|\mathbf{x} - \mathbf{y}|} + f_{xc}^N(\mathbf{x}, \mathbf{y}) \right) n_1(\mathbf{y}) \right] \]  

(2.115)

and

\[ \chi_1(\mathbf{r}, \mathbf{r}') = \int d^3x \int d^3x' \Xi_s^N \left[ \Delta_1(\mathbf{x}, \mathbf{x}') - \int d^3y \int d^3y' f_{xc}^N(\mathbf{x}, \mathbf{x}', \mathbf{y}, \mathbf{y}') \chi_1(\mathbf{y}, \mathbf{y}') \right] \]  

(2.116)

with

\[ f_{xc}^N(\mathbf{x}, \mathbf{x}', \mathbf{y}, \mathbf{y}') := -\frac{\delta \Delta_{xc}(\mathbf{x}, \mathbf{x}')}{\delta \chi(\mathbf{y}, \mathbf{y}')}. \]  

(2.117)

Since Eq. (2.115) does not involve the superconducting order parameter, the phase transition into the superconducting phase is completely described by Eq. (2.116). For \( T < T_c \) an infinitesimal perturbation \( \chi_1(\mathbf{r}, \mathbf{r}') \) leads to a finite order parameter \( \chi_1(\mathbf{r}, \mathbf{r}') \). Eq. (2.116) can be rewritten in the form

\[ \left[ 1 + \int \int \Xi_s^N f_{xc}^N \right] \chi_1 = \int \Xi_s^N \Delta_1. \]  

(2.118)

Since \( \chi_1 \) is finite while the right-hand side remains infinitesimal, the integral operator \([1 + \int \int \Xi_s^N f_{xc}^N]\) has to have an eigenvalue 0. Hence:

\[ -\int \Xi_s^N f_{xc}^N \chi = \chi \]  

(2.119)

Operating with \( \int f_{xc} \ldots \) on this equation and identifying \( \Delta = \int f_{xc} \chi \) this yields:

\[ -\int d^3x \int d^3x' \int d^3y \int d^3y' f_{xc}^N(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Xi_s^N(\mathbf{x}, \mathbf{x}', \mathbf{y}, \mathbf{y}') \Delta(\mathbf{y}, \mathbf{y}') = \Delta(\mathbf{r}, \mathbf{r'}). \]  

(2.120)

This equation can be transformed into the Bloch representation. With the explicit form of the response function \( \Xi_s^N \) [34, 35, 18]

\[ \Xi_s^N(\mathbf{r}, \mathbf{r}'; \mathbf{x}, \mathbf{x}') = -\sum_{ij} \frac{f_\beta((\epsilon_j - \mu)) - f_\beta((\epsilon_i - \mu))}{(\epsilon_j - \mu) + (\epsilon_i - \mu)} \varphi_i(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{x}) \varphi_j(\mathbf{x}') \]  

(2.121)
one obtains:

\[ \Delta_{k,k'} = -\sum_{q,q'} f^{N\text{xc}}_{\lambda}(k,k';q,q') \frac{f_{\beta}(-\epsilon_q - \mu) - f_{\beta}(\epsilon_{q'} - \mu)}{(\epsilon_q - \mu) + (\epsilon_{q'} - \mu)} \Delta_{q,q'} \]  \hfill (2.122)

or, using the symmetry properties, given in appendix A:

\[ \Delta(n,n',k) = -\sum_{m,m',q} f^{N\text{xc}}_{\lambda}(n,n',m,m';q) \frac{f_{\beta}(-\epsilon_{mq} - \mu) - f_{\beta}(\epsilon_{m'q} - \mu)}{(\epsilon_{mq} - \mu) + (\epsilon_{m'q} - \mu)} \Delta(m,m',q). \]  \hfill (2.123)

It should be stressed, that this equation gives an exact description of the superconducting phase transition for a system with a given Hamiltonian \( \hat{H} \), provided that the exact kernel \( f^{N\text{xc}}_{\lambda} \) is known.

It is now easily recognized that the decoupling approximation discussed in section 2.6 is equivalent to neglecting the off-diagonal elements of the interaction, i.e.:

\[ f^{\text{decoupling}}_{\text{xc}}(n,n',k; m,m',q) = \delta_{n,n'} \delta_{m,m'} f_{\text{xc}}(n,n',k; m,m',q). \]  \hfill (2.124)

In this case, Eq. (2.123) reduces to the decoupled, linearized gap equation (2.107).
Chapter 3

Perturbation expansion for the xc terms

3.1 Unperturbed system

In this section, a perturbation theory for the superconducting state of an electron-phonon system will be developed as a generalization of the KS perturbation theory for superconductors by S. Kurth [17] to systems including phonons. The unperturbed system consists of non-interacting, but superconducting KS electrons and non-interacting phonons. Thus the phononic part only contains the ion-ion interaction up to second order in the expansion around the equilibrium positions. The explicit terms of this expansion are given in the next section. The respective order of a term is indicated by the superscribed number. All remaining terms are treated as perturbation. Therefore:

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$ (3.1)

with the unperturbed system

$$\hat{H}_0 = \hat{T}_i + \hat{U}^{ii(0,1,2)} + \int \hat{\Gamma} V_H^{\epsilon i(0,1,2)} + \int \hat{\Gamma} V_{xc}^{\epsilon i(0,1,2)}$$

$$+ \hat{T}^e + \int \hat{n} (v_H^{ee} + v_H^{ei} + v_{xc}) - \int (\hat{\chi}^\dagger \Delta_{xc} + h.c.)$$ (3.2)

and the perturbation

$$\hat{H}_1 = \hat{U}^{ei} - \int \hat{\Gamma} V_H^{\epsilon i(0,1,2)} - \int \hat{\Gamma} V_{xc}^{\epsilon i(0,1,2)} + \hat{U}^{ii(3,...)}$$

$$+ \hat{U}^{ee} - \int \hat{n} (v_H^{ee} + v_H^{ei} + v_{xc}) + \int (\hat{\chi}^\dagger \Delta_{xc} + h.c.) .$$ (3.3)

The grand canonical potential of the system described by $\hat{H}_0$ is given by:

$$\Omega_0[n, \chi, \Gamma] = \left( T^s + U^{ii(0,1,2)} + \int \Gamma V_H^{\epsilon i(0,1,2)} + \int \Gamma V_{xc}^{\epsilon i(0,1,2)} \right)$$

$$+ \left( T^e + \int n(v_H^{ee} + v_H^{ei} + v_{xc}) - \int (\chi^\dagger \Delta_{xc} + h.c.) - \frac{1}{\beta} S_s. \right.$$ (3.4)
Chapter 3. Perturbation expansion for the xc terms

The difference \( \Delta \Omega = \Omega - \Omega_0 \) can be calculated diagrammatically. By comparing Eq. (3.4) to Eq. (2.38) the exchange-correlation functional \( F_{xc}[n, \chi, \Gamma] \) can be expressed as:

\[
F_{xc}[n, \chi, \Gamma] = \Delta \Omega - U^{ii, (3\ldots)} - E_{ee}^{\chi}[n] - E_{ee}^{\chi}[n, \Gamma] + \int GV_{xc}^{\chi(0,1,2)} + \int n(\nu_{ee}^{\chi} + \nu_{ei}^{\chi} + \nu_{xc}) - \int \left( \chi^* \Delta_{xc} + h.c. \right)
\]

\[
= \Delta \Omega - U^{ii, (3\ldots)} + \int GV_{xc}^{\chi(0,1,2)} + \int GV_{xc}^{\chi(0,1,2)} + \frac{1}{2} \int n v_{H} + \int n v_{xc} - \int \left( \chi^* \Delta_{xc} + h.c. \right).
\]

(3.5)

### 3.2 Harmonic expansion around the equilibrium

At temperatures well below the melting point of a solid, the ions are well localized and vibrating around their equilibrium positions. Therefore it is sufficient to expand all quantities which contain the ionic coordinates around the equilibrium configuration. The expansion is completely analogous to the one employed in section 2.4 to calculate the phonons.

The electron-ion coupling term is:

\[
\hat{U}_{ei} = -\sum_{\sigma} \int d^3r \sum_{\alpha,i} Z_{\alpha} \frac{\hat{\Psi}_{\sigma}^\dagger(r)\hat{\Psi}_{\sigma}(r)}{|r - R_{\alpha,i}|},
\]

(3.6)

where again the second quantization is used only for the electronic degrees of freedom while the ions are treated in first quantization. Its zero-order component represents the interaction of the electrons with the static ion lattice:

\[
\hat{U}_{ei}^{(0)} = -\sum_{\sigma} \int d^3r \sum_{\alpha,i} Z_{\alpha} \frac{\hat{\Psi}_{\sigma}^\dagger(r)\hat{\Psi}_{\sigma}(r)}{|r - R_{\alpha,i}^0|} = \sum_{\sigma} \int d^3r \hat{\Psi}_{\sigma}^\dagger(r)\hat{\Psi}_{\sigma}(r) v_{\text{latt}}(r),
\]

(3.7)

where the equilibrium positions \( R_{\alpha,i}^0 \) are defined by Eq. (2.53). The first-order term is the electron-phonon interaction

\[
\hat{U}_{ei}^{(1)} = \sum_{\lambda,q} \sum_{\sigma} \int d^3r \hat{\Psi}_{\sigma}^\dagger(r)\hat{\Psi}_{\sigma}(r)V_{\lambda,q}(r)\hat{\Phi}_{\lambda,q}
\]

(3.8)

with

\[
V_{\lambda,q}(r) = \sum_{\alpha,i,d} \frac{Z_{\alpha}}{\sqrt{M_{\alpha}}^{\lambda_{q}}} e^{i\xi_{\alpha,i,d}(\lambda_{q})} \left( \partial_{\mu} \frac{1}{|r - R_{\alpha,i}|} \right).
\]

(3.9)

The second-order term describes an interaction involving two phonons:

\[
\hat{U}_{ei}^{(2)} = \sum_{\lambda_{q};\lambda'_{q'}} \sum_{\sigma} \int d^3r \hat{\Psi}_{\sigma}^\dagger(r)\hat{\Psi}_{\sigma}(r)V_{\lambda_{q},\lambda'_{q'}}^{(2)}(r)\hat{\Phi}_{\lambda_{q},\lambda'_{q'}}\hat{\Phi}_{\lambda'_{q'},}\]

(3.10)
3.2. Harmonic expansion around the equilibrium

where

$$V_{\lambda q;\lambda',q'}^{(2)}(r) = - \sum_{\alpha,\beta,\mu,\mu'} \frac{Z_a^2}{2M_\alpha \sqrt{\Omega_a q q'}} e^{i(q+q') \mathbf{R}_{\alpha_0,\mu}^{0}} \zeta^{(\alpha,\mu)}(r,\mathbf{R}) \zeta^{(\alpha',\mu')}(r,\mathbf{R}') \left( \partial_{\mu} \partial_{\mu'} \frac{1}{|\mathbf{r} - \mathbf{R}_{a_0,\mu}|} \right).$$

(3.11)

The Hartree term acting on the ions is:

$$\int \hat{V}_H^{ei} = - \frac{1}{2m} \sum_{\alpha,\alpha'} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \int d^3 \mathbf{r} \hat{\Gamma}_{\alpha,\alpha'}(\mathbf{R}, \mathbf{R}') \times$$

$$\left( \frac{Z_\alpha}{N_{\alpha'} + \zeta_{\alpha'} \delta_{\alpha,\alpha'}} \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}|} + \frac{Z_{\alpha'}}{N_\alpha + \zeta_\alpha \delta_{\alpha,\alpha'}} \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}'|} \right) = - \sum_{\alpha,i} \int d^3 \mathbf{r} \frac{Z_\alpha n(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_{a,i}|}.$$  

(3.12)

Its harmonic coefficients are:

$$\int \hat{V}_H^{ext,(0)} = \int d^3 \mathbf{r} n(\mathbf{r}) n_{latt}(\mathbf{r})$$  

(3.13)

$$\int \hat{V}_H^{ext,(1)} = \sum_{\lambda,\mathbf{q}} V_{H,\lambda,\mathbf{q}}^{(1)} \hat{\Phi}_{\lambda,\mathbf{q}}$$  

(3.14)

$$\int \hat{V}_H^{ext,(2)} = \sum_{\lambda,\mathbf{q},\lambda',\mathbf{q}'} V_{H,\lambda,\mathbf{q};\lambda',\mathbf{q}'}^{(2)} \hat{\Phi}_{\lambda,\mathbf{q}} \hat{\Phi}_{\lambda',\mathbf{q}'}$$  

(3.15)

with

$$V_{H,\lambda,\mathbf{q}}^{(1)} = \int d^3 \mathbf{r} n(\mathbf{r}) V_{\lambda,\mathbf{q}}(\mathbf{r})$$  

(3.16)

$$V_{H,\lambda,\mathbf{q};\lambda',\mathbf{q}'}^{(2)} = \int d^3 \mathbf{r} n(\mathbf{r}) V_{\lambda,\mathbf{q};\lambda',\mathbf{q}'}(\mathbf{r})$$  

(3.17)

The ionic exchange-correlation term is

$$\int \hat{V}_{xc}^{ei} = \sum_{\alpha,\alpha'} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \hat{\Gamma}_{\alpha,\alpha'} V_{xc,\alpha,\alpha'}(\mathbf{R}, \mathbf{R}')$$

$$= \frac{1}{2} \sum_{\alpha,i \neq \alpha',i'} V_{xc,\alpha,\alpha'}(\mathbf{R}_{a,i}, \mathbf{R}_{a',i'}).$$  

(3.18)

Its small-deviation expansion is

$$\hat{V}_{xc}^{ei(0)} = \frac{1}{2} \sum_{\alpha,i \neq \alpha',i'} V_{xc,\alpha,\alpha'}(\mathbf{R}_{a,i}^0, \mathbf{R}_{a',i'}^0)$$  

(3.19)

$$\hat{V}_{xc}^{ei(1)} = \sum_{\lambda,\mathbf{q}} V_{xc,\lambda,\mathbf{q}}^{(1)} \hat{\Phi}_{\lambda,\mathbf{q}}$$  

(3.20)

$$\hat{V}_{xc}^{ei(2)} = \sum_{\lambda,\mathbf{q}} V_{xc,\lambda,\mathbf{q};\lambda',\mathbf{q}'}^{(2)} \hat{\Phi}_{\lambda,\mathbf{q}} \hat{\Phi}_{\lambda',\mathbf{q}'}.$$  

(3.21)
Finally, the expansion of
\[
\int \Gamma V_{xc}^{ei} = \sum_{\alpha,\alpha'} \int d^3 R \int d^3 R' \Gamma_{\alpha,\alpha'}(R, R') V_{xc,\alpha,\alpha'}(R, R')
\] (3.22)
yields:
\[
\int \Gamma V_{xc}^{ei(0)} = \frac{1}{2} \sum_{(\alpha,i) \neq (\alpha',i')} V_{xc,\alpha,\alpha'}(R^0_{\alpha,i}, R^0_{\alpha',i'})
\] (3.23)
\[
\int \Gamma V_{xc}^{ei(1)} = \sum_{\lambda, q} V_{xc,\lambda q}^{(1)} \langle \hat{\Phi}_{\lambda, q} \rangle
\]
\[
\int \Gamma V_{xc}^{ei(2)} = \sum_{\lambda, q} V_{xc,\lambda q,\lambda', q'}^{(2)} \langle \hat{\Phi}_{\lambda, q} \hat{\Phi}_{\lambda', q'} \rangle.
\] (3.24)

To evaluate the expectation-values of the phonon-operators in the last terms, we inspect the term before performing the expansion.
\[
\int \Gamma V_{xc}^{ei} = \sum_{\alpha,\alpha'} \int d^3 R \int d^3 R' \Gamma_{\alpha,\alpha'}(R, R') V_{xc,\alpha,\alpha'}(R, R')
\]
\[
= \sum_{\alpha,\alpha'} \int d^3 R \int d^3 R' \langle \hat{\Gamma}_{\alpha,\alpha'}(R, R') \rangle V_{xc,\alpha,\alpha'}(R, R')
\] (3.25)

By construction, the diagonal of the two-particle density-matrix \(\Gamma_{\alpha,\alpha'}(R, R')\) equals that of the KS system. Hence
\[
\langle \hat{\Gamma}_{\alpha,\alpha'}(R, R') \rangle = \langle \hat{\Gamma}_{\alpha,\alpha'}(R, R') \rangle_{KS}.
\] (3.26)

If now \(\Gamma_{\alpha,\alpha'}(R, R')\) is expanded, one sees immediately that the resulting expectation values can be evaluated with respect to the KS system. Since in the non-interacting KS system the particle number is conserved, we find
\[
\langle \hat{\Phi}_{\lambda, q} \rangle = 0.
\] (3.27)

The other expectation value can be identified with the equal-time limit of the KS phonon Green’s function
\[
\langle \hat{\Phi}_{\lambda, q} \hat{\Phi}_{\lambda', q'} \rangle = -\delta_{\lambda,\lambda'} \delta_{q, q'} D_{\lambda, q}(\tau, \tau^+)
\] (3.28)
and can be evaluated\(^1\) to result in
\[
-D_{\lambda, q}(\tau, \tau^+) = (2n_{\beta}(\Omega_{\lambda q}) + 1).
\] (3.29)

Here, \(n_{\beta}(\Omega)\) is the Bose distribution function. Hence we get:
\[
\int \Gamma V_{xc}^{ei(1)} = 0
\]
\[
\int \Gamma V_{xc}^{ei(2)} = \sum_{\lambda, q} V_{xc,\lambda q,\lambda', q'}^{(2)} (2n_{\beta}(\Omega_{\lambda q}) + 1).
\] (3.30)

\(^1\)see appendix B.
Keeping only terms up to harmonic order, the perturbation in (3.1) is:

\[
\hat{H}_{1}^{(0,1,2)} = \left( \sum_{\sigma} \frac{1}{2} \int d^{3}r \int d^{3}r' \frac{\hat{\Psi}_{\sigma}(r) \hat{\Psi}_{\sigma}^{\dagger}(r') \hat{\Psi}_{\sigma}(r') \hat{\Psi}_{\sigma}(r)}{|r-r'|} \right)
+ \sum_{\sigma} \int d^{3}r \hat{\Psi}_{\sigma}(r) v_{\text{lat}}(r) \\
+ \sum_{\lambda, q} \sum_{\sigma} \int d^{3}r \hat{\Psi}_{\sigma}(r) \hat{\Phi}_{\lambda, q}(r) V_{\lambda, q}(r) \hat{\Phi}_{\lambda, q} \\
+ \sum_{\lambda, q, \lambda', q'} \sum_{\sigma} \int d^{3}r \hat{\Psi}_{\sigma}(r) \hat{\Phi}_{\lambda, q}(r) V^{(2)}_{\lambda, q, \lambda', q'}(r) \hat{\Phi}_{\lambda, q} \hat{\Phi}_{\lambda', q'} \\
- \left( \sum_{\sigma} \int d^{3}r \hat{\Psi}_{\sigma}(r) \hat{\Phi}_{\sigma}(r) \left( v^{(1)}_{\text{H}}(r) + v^{(1)}_{\text{I}}(r) + v_{\text{xc}}(r) \right) \right) \\
- \int d^{3}r \int d^{3}r' \left( \hat{\Psi}_{\sigma}(r) \hat{\Psi}_{\sigma}^{\dagger}(r') \Delta_{\text{xc}}^{\ast}(r, r') + h.c. \right) \\
- \left( \int d^{3}r n(r) v_{\text{lat}}(r) + \sum_{\lambda, q} V^{(1)}_{\text{H}, \lambda, q}(r) \hat{\Phi}_{\lambda, q} + \sum_{\lambda, q, \lambda', q'} V^{(2)}_{\text{xc}, \lambda, q, \lambda', q'}(r) \hat{\Phi}_{\lambda, q} \hat{\Phi}_{\lambda', q'} \right) \\
- \left( \frac{1}{2} \sum_{(\alpha, i) \neq (\alpha', i')} V_{\text{xc}, \alpha, \alpha'}(R_{\alpha, i}^{0}, R_{\alpha', i'}^{0}) \right) \\
+ \sum_{\lambda, q} V^{(1)}_{\text{xc}, \lambda, q}(r) \hat{\Phi}_{\lambda, q} + \sum_{\lambda, q, \lambda', q'} V^{(2)}_{\text{xc}, \lambda, q, \lambda', q'}(r) \hat{\Phi}_{\lambda, q} \hat{\Phi}_{\lambda', q'}. \tag{3.31}
\]

In principle, higher-order terms could be treated in a similar way.

### 3.3 Many-body perturbation theory

Having identified the perturbation in Eq. (3.1), we are now going to develop a many-body perturbation theory for this Hamiltonian. This will ultimately lead to explicit expression for the xc functionals.

The difference in the grand canonical potential \( \Delta \Omega \) can be evaluated by many-body perturbation theory.

\[
\Delta \Omega = -\frac{1}{\beta} \left( \ln(Z_{G}) - \ln(Z_{G}^{0}) \right) \tag{3.32}
\]

where \( Z_{G} \) is the grand canonical partition function

\[
Z_{G} = \text{Tr} \{ e^{-\beta \hat{H}} \}. \tag{3.33}
\]

\( Z_{G}^{0} \) is the corresponding partition function of the non-interacting system.

We define the Heisenberg and interaction "pictures":

\[
\hat{O}_{H}(\tau) = e^{\hat{H}_{0} \tau} \hat{O} e^{-\hat{H}_{0} \tau}, \tag{3.34}
\]
\[
\hat{O}_{I}(\tau) = e^{\hat{H}_{0} \tau} \hat{O} e^{-\hat{H}_{0} \tau}. \tag{3.35}
\]
Chapter 3. Perturbation expansion for the xc terms

The two “pictures” can be related to each other via

\[ \hat{O}_H(\tau) = \hat{U}(0, \tau) \hat{O}_I(\tau) \hat{U}(\tau, 0) \] (3.36)

where \( \hat{U} \) is the time\(^2 \) evolution operator

\[ \hat{U}(\tau, \tau') = e^{\hat{H}_0 \tau} e^{-\hat{H}(\tau-\tau')} e^{-\hat{H}_0 \tau'} \] (3.37)

which has the properties

\[ \hat{U}(\tau_1, \tau_2) \hat{U}(\tau_2, \tau_3) = \hat{U}(\tau_1, \tau_3) \] (3.38)

and

\[ \hat{U}(\tau_1, \tau_1) = 1. \] (3.39)

Its time dependence is governed by the equation of motion:

\[ \frac{\partial}{\partial \tau} \hat{U}(\tau, \tau') = -\hat{H}_I(\tau) \hat{U}(\tau, \tau'). \] (3.40)

This can formally be solved by

\[ \hat{U}(\tau, \tau') = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_{\tau'}^{\tau} d\tau_1 \ldots \int_{\tau'}^{\tau} d\tau_n \hat{T} \left( \hat{H}_I(\tau_1) \ldots \hat{H}_I(\tau_n) \right) \] (3.41)

where \( \hat{T} \) is the time-ordering operator defined by

\[ \hat{T} \left( \hat{A}(\tau) \hat{B}(\tau') \right) = \begin{cases} \hat{A}(\tau) \hat{B}(\tau') & \text{for } \tau > \tau' \\
-\hat{B}(\tau') \hat{A}(\tau) & \text{for } \tau < \tau' \end{cases} \] (3.42)

for Fermions and by

\[ \hat{T} \left( \hat{a}(\tau) \hat{b}(\tau') \right) = \begin{cases} \hat{a}(\tau) \hat{b}(\tau') & \text{for } \tau > \tau' \\
\hat{b}(\tau') \hat{a}(\tau) & \text{for } \tau < \tau' \end{cases} \] (3.43)

for Bosons. Using this time-evolution operator, one can write

\[ \frac{Z_G}{Z_G^0} = \frac{1}{Z_G^0} \text{Tr} \left\{ e^{-\beta \hat{H}} \right\} = \frac{1}{Z_G^0} \text{Tr} \left\{ e^{-\beta \hat{H}_0} \hat{U}(\beta, 0) \right\} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta d\tau_1 \ldots \int_0^\beta d\tau_n \text{Tr} \left\{ \rho^0 \hat{T} \left( \hat{H}_I(\tau_1) \ldots \hat{H}_I(\tau_n) \right) \right\}. \] (3.44)

The trace can then be evaluated with the help of Wick’s theorem. In the present case, \( \hat{H}_I \) contains both Fermionic and Bosonic operators. Since the Bosonic operators commute with the Fermionic operators, they can be grouped together:

\[ \text{Tr} \left\{ \rho^0 \hat{T} \hat{A}(\tau_1) \hat{B}(\tau_2) \hat{a}(\tau_3) \hat{C}(\tau_4) \hat{b}(\tau_5) \hat{D}(\tau_6) \ldots \right\} = \] \[ = \text{Tr} \left\{ \rho^0 (\hat{T} \hat{A}(\tau_1) \hat{B}(\tau_2) \hat{C}(\tau_4) \hat{D}(\tau_6) \ldots) (\hat{T} \hat{a}(\tau_3) \hat{b}(\tau_5) \ldots) \right\}. \] (3.45)

\(^2\)in the following the expression “time” will be used for the imaginary time \( \tau \).
3.3. Many-body perturbation theory

Because in the non-interacting system the electrons and phonons are completely decoupled, we can write $\hat{\rho}^0 = \hat{\rho}_{el}^0 \hat{\rho}_{ph}^0$. The eigenstates of the non-interacting system are product states of an electronic and a phononic state. Thus we can continue

$$
= \text{Tr} \left\{ \hat{\rho}_{el}^0 (\hat{T} \hat{A}^\dagger (\tau_1) \hat{B} (\tau_2) \hat{C}^\dagger (\tau_4) \hat{D} (\tau_6) \ldots) \right\} \text{Tr} \left\{ \hat{\rho}_{ph}^0 (\hat{T} \hat{a}^\dagger (\tau_3) \hat{b} (\tau_5) \ldots) \right\}
$$

$$
= \left( \sum \text{all Fermi-contractions} \right) \left( \sum \text{all phonon-contractions} \right).
$$

In the last step, we used the result of Wick’s theorem for Bogolons as proven in [16]. This replaces Wick’s theorem for Fermions, which is not valid in this form in the superconducting state, and leads to the additional anomalous contractions defined below. Wick’s theorem for Bosons as shown in [36] is still valid in superconducting systems. The non-vanishing contractions are:

$$
\text{Tr} \left\{ \hat{\rho}_{el}^0 \hat{T} \hat{\Psi}_\sigma^\dagger (r, \tau) \hat{\Psi}^\dagger_{\sigma'} (r', \tau') \right\} = -G_{\sigma,\sigma'}^0 (r, \tau; r', \tau')
$$

(3.47)

$$
\text{Tr} \left\{ \hat{\rho}_{ph}^0 \hat{T} \hat{\Phi}_{\lambda,q}^\dagger (\tau_3) \hat{\Phi}_{\lambda,q}^\dagger (\tau') \right\} = -\delta_{\lambda,\lambda'} \delta_{q,q'} D_{\lambda,q}^0 (\tau; r, r'; \tau')
$$

(3.50)

Since the Hamiltonian does not depend explicitly on time, the Green’s functions depend only on the difference $(\tau - \tau')$ and can thus be expanded in Fourier series:

$$
G_{\sigma,\sigma'}^0 (r, r'; \tau - \tau') = \frac{1}{\beta} \sum_n e^{-i\omega_n (\tau - \tau')} G_{\sigma,\sigma'}^0 (r, r'; \omega_n)
$$

(3.51)

$$
F_{\sigma,\sigma'}^0 (r, r'; \tau - \tau') = \frac{1}{\beta} \sum_n e^{-i\omega_n (\tau - \tau')} F_{\sigma,\sigma'}^0 (r, r'; \omega_n)
$$

(3.52)

$$
D_{\lambda,q}^0 (\tau - \tau') = \frac{1}{\beta} \sum_\nu e^{-i\omega_\nu (\tau - \tau')} D_{\lambda,q}^0 (\omega_\nu)
$$

(3.53)

with the Fermionic Matsubara frequencies

$$
\omega_n = \frac{(2n + 1)\pi}{\beta}
$$

(3.54)

and the Bosonic Matsubara frequencies for the phonons

$$
\omega_\nu = \frac{2\nu\pi}{\beta}.
$$

(3.55)

The Fourier transforms of the Green’s functions are:

$$
G_{\sigma,\sigma'}^0 (r, r'; \omega_n) = \delta_{\sigma,\sigma'} \sum_i \left( \frac{u_i (r) u_i^* (r')}{i\omega_n - E_i} + \frac{v_i (r) v_i^* (r')}{i\omega_n + E_i} \right)
$$

(3.56)

---

3. This definition of the anomalous Green’s functions differs from the one, given in [17]. The reason for the new definition is given in appendix B.

4. See appendix B.
3.4 Feynman rules

All terms appearing in the above perturbation expansion (3.44) can be constructed diagrammatically. Since the rules for their construction differ slightly from the ordinary Feynman rules, we will briefly derive and describe them in this section.

The total perturbation $\hat{H}_1$ can be broken up into the different constituents denoted by $\hat{H}_{1,(i)}$:

$$\hat{H}_1 = \sum_{i=1}^{m} \hat{H}_{1,(i)}. \quad (3.60)$$

Each of these constituents represents a different physical process. The $n$th order term then formally looks like:

$$\left(\hat{H}_1\right)^n = \sum_{n_1+n_2+\ldots+n_m=n} \frac{n!}{n_1!n_2!\ldots n_m!} (\hat{H}_{1,1})^{n_1} (\hat{H}_{1,2})^{n_2} \ldots (\hat{H}_{1,m})^{n_m} \quad (3.61)$$

For each term of the sum, we draw $n_i$ times the graphical element representing $\hat{H}_{1,(i)}$.

These elements are:

- the Coulomb interaction

$$\frac{1}{2} \frac{1}{|\mathbf{r} - \mathbf{r}'|} = \begin{array}{c} \mathbf{r} \sigma \\ \rightarrow \\ \mathbf{r}' \sigma' \end{array} \quad (3.62)$$

Since the Coulomb interaction is treated as an instantaneous interaction, the Green’s functions attached to it have to be taken at the same argument $\tau$.

- the terms arising from the electron-ion coupling

- 0th order: the lattice potential

$$v_{\text{latt}}(\mathbf{r}) = \begin{array}{c} \mathbf{r} \sigma \\ \rightarrow \\ 0 \end{array} \quad (3.63)$$
3.4. Feynman rules

- 1\textsuperscript{st} order: electron-phonon coupling

\[ V_{\lambda, \mathbf{q}}(\mathbf{r}) = \mathbf{r} \sigma \quad \lambda, \mathbf{q} \]  
\hspace{1cm} (3.64)

- 2\textsuperscript{nd} order: coupling to two phonons

\[ V^{(2)}_{\lambda, \mathbf{q}; \lambda', \mathbf{q}'}(\mathbf{r}) = \mathbf{r} \sigma \quad \lambda, \mathbf{q} \]  
\hspace{1cm} (3.65)

- the “external” potentials, coupling to the electronic density:

- the electronic Hartree potential

\[ -v_{\text{H}}^{ee}(\mathbf{r}) = \mathbf{r} \sigma \quad \text{H} \]  
\hspace{1cm} (3.66)

- the electron-ion Hartree potential

\[ -v_{\text{H}}^{ie}(\mathbf{r}) = \mathbf{r} \sigma \quad \text{ie} \]  
\hspace{1cm} (3.67)

- the exchange-correlation potential for the electrons

\[ -v_{\text{xc}}(\mathbf{r}) = \mathbf{r} \sigma \quad \text{xc} \]  
\hspace{1cm} (3.68)

- the pair potentials coupling to the anomalous density

\[ -\frac{1}{2} \delta_{\sigma, -\sigma'} \Delta_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \mathbf{r}, \sigma \quad \mathbf{r}', \sigma' \]  
\hspace{1cm} (3.69)

and

\[ -\frac{1}{2} \delta_{\sigma, -\sigma'} \Delta^{*}_{\text{xc}}(\mathbf{r}, \mathbf{r}') = \mathbf{r}, \sigma \quad \mathbf{r}', \sigma' \]  
\hspace{1cm} (3.70)

The pair potentials are, similar to the Coulomb interaction, “local” in the imaginary time.
• the Hartree potential for the ions
  
  - 0th order:
    \[ -\int d^3r \, n(r) \, v_{\text{att}}(r) = \begin{array}{c} \text{H} \end{array} \quad (3.71) \]

  This term is a constant and cannot be connected to any other element of the diagrammatics.

  - 1st order:
    \[ -V^{(1)}_{H,\lambda,q} = \begin{array}{c} \text{H} \end{array} \quad (3.72) \]

  - 2nd order:
    \[ -V^{(2)}_{H,\lambda,q;\lambda',q'} = \begin{array}{c} \text{H} \end{array} \quad (3.73) \]

• the correlation-potential for the ions

  - 0th order:
    \[ \frac{1}{2} \sum_{(\alpha,i) \neq (\alpha',i')} V_{\text{xc},\alpha,\alpha'}(R_0^{\alpha,i}, R_0^{\alpha',i'}) = \begin{array}{c} \text{xc} \end{array} \quad (3.74) \]

  Also this zeroth order term is constant.

  - 1st order:
    \[ -V^{(1)}_{\text{xc},\lambda,q} = \begin{array}{c} \text{xc} \end{array} \quad (3.75) \]

  - 2nd order:
    \[ -V^{(2)}_{\text{xc},\lambda,q;\lambda',q'} = \begin{array}{c} \text{xc} \end{array} \quad (3.76) \]

These elements have to be connected in all possible ways, using the Green’s functions of the non-interacting electron-phonon system, which are represented as:
Green’s functions with equal imaginary times have to be interpreted as:

\[ G(r, \tau; r', \tau') = \lim_{\eta 	o 0^+} G(r, \tau; r', \tau + \eta). \]  

Diagrams, which cannot be closed in a certain order, are not taken into account since their contribution vanishes due to particle conservation of the non-interacting system. The prefactors of each term are\(^5\)

\[ \frac{(-1)^n}{n!} \frac{(-1)^q+p}{n_1! n_2! \ldots n_m!} = \frac{(-1)^{n+q+p}}{n_1! n_2! \ldots n_m!}, \]  

where \( n \) is the total order of the diagram, \((n_1, \ldots, n_m)\) are the “partial” orders with respect to \( \hat{H}_{1,(i)} \), \( q \) is the number of closed Fermion loops in the diagram and \( p \) is the number of pairs of anomalous Green’s functions. From (3.46) follows:

\[ \frac{Z_G}{Z_0} = \sum (\text{all diagrams}). \]  

The derivation of the linked cluster theorem is in complete analogy to the one in conventional many-body perturbation theory [37]. Consider two arbitrary graphs\(^6\) with the partial orders \((n_1, n_2, \ldots, n_m)\) and \((\tilde{n}_1, \tilde{n}_2, \ldots, \tilde{n}_m)\), denoted by

\[ \gamma(n_1, n_2, \ldots, n_m) \quad \text{and} \quad \tilde{\gamma}(\tilde{n}_1, \tilde{n}_2, \ldots, \tilde{n}_m). \]

\(^5\)see Appendix C.

\(^6\)Here we distinguish a diagram, which includes all prefactors, from a graph, which is understood as the plain translation of the diagrammatic elements.
The terms in the perturbation expansion corresponding to these graphs are:

\[ g(n_1, n_2, \ldots, n_m) = \frac{(-1)^{n+q+p}}{n_1! n_2! \ldots n_m!} \gamma(n_1, n_2, \ldots, n_m) \]

and

\[ \tilde{g}(\tilde{n}_1, \tilde{n}_2, \ldots, \tilde{n}_m) = \frac{(-1)^{\tilde{n}+\tilde{q}+\tilde{p}}}{\tilde{n}_1! \tilde{n}_2! \ldots \tilde{n}_m!} \tilde{\gamma}(\tilde{n}_1, \tilde{n}_2, \ldots, \tilde{n}_m). \]

The graph which consists of the two constituents \( \gamma \) and \( \tilde{\gamma} \) contributes

\[ \frac{(-1)^{(n+\tilde{n})+(q+\tilde{q})+(p+\tilde{p})}}{(n_1 + \tilde{n}_1)! (n_2 + \tilde{n}_2)! \ldots (n_m + \tilde{n}_m)!} \left( \gamma(n_1, n_2, \ldots, n_m) \tilde{\gamma}(\tilde{n}_1, \tilde{n}_2, \ldots, \tilde{n}_m) \right) \]

to the expansion series. Thus one finds the relation

\[ \left( g(n_1, n_2, \ldots, n_m) \tilde{g}(\tilde{n}_1, \tilde{n}_2, \ldots, \tilde{n}_m) \right) = \]

\[ = \frac{(n_1! n_2! \ldots n_m!)(\tilde{n}_1! \tilde{n}_2! \ldots \tilde{n}_m!)}{(n_1 + \tilde{n}_1)! (n_2 + \tilde{n}_2)! \ldots (n_m + \tilde{n}_m)!} \left( g(n_1, n_2, \ldots, n_m) \right) \left( \tilde{g}(\tilde{n}_1, \tilde{n}_2, \ldots, \tilde{n}_m) \right). \]

(3.84)

An arbitrary unlabeled graph can be classified by its linked subgraphs and their multiplicity. A graph which contains \( k_1 \) times the subgraph \( \gamma_1(n_1^{(1)}, n_2^{(1)}, \ldots, n_m^{(1)}) \), \( k_2 \) times \( \gamma_2(n_1^{(2)}, n_2^{(2)}, \ldots, n_m^{(2)}) \), \ldots contributes according to Eq. (3.84):

\[ \left( k_1 \times g_1(n_1^{(1)}, n_2^{(1)}, \ldots, n_m^{(1)}), k_2 \times g_2(n_1^{(2)}, n_2^{(2)}, \ldots, n_m^{(2)}), \ldots \right) = \]

\[ = \frac{(n_1^{(1)}! n_2^{(1)}! \ldots n_m^{(1)}!)(n_1^{(2)}! n_2^{(2)}! \ldots n_m^{(2)}!)^{k_2} \ldots}{(n_1^{(1)} + n_2^{(1)} + \ldots)! (n_1^{(2)} + n_2^{(2)} + \ldots)! \ldots (n_m^{(1)} + n_m^{(2)} + \ldots)!} (g_1) (g_2) \ldots. \]  

(3.85)

The total number of such graphs is

\[ (k_1 n_1^{(1)} + k_2 n_2^{(2)} + \ldots)! (k_1 n_2^{(1)} + k_2 n_2^{(2)} + \ldots)! \ldots \]

since only diagrammatic elements of the same type can be interchanged. But interchanging elements within a linked subgraph leads to equivalent expressions and thus these permutations, which are

\[ (n_1^{(1)}! n_2^{(1)}! \ldots n_m^{(1)}!)^{k_1} (n_1^{(2)}! n_2^{(2)}! \ldots n_m^{(2)}!)^{k_2} \ldots \]

must not be counted. Also the \( k_1 k_2 \ldots \) possibilities of exchanging whole subgraphs do not lead to new expressions. The number of distinct graphs is thus:

\[ \frac{(k_1 n_1^{(1)} + k_2 n_2^{(2)} + \ldots)! (k_1 n_2^{(1)} + k_2 n_2^{(2)} + \ldots)! \ldots}{(k_1 n_1^{(1)} + k_2 n_1^{(2)} + \ldots)! (k_1 n_2^{(1)} + k_2 n_2^{(2)} + \ldots)! \ldots (k_1 k_2 \ldots)}. \]

(3.86)

The sum over all diagrams is

\[ \frac{Z_G}{Z_G^0} = \sum \text{all diagrams} = \sum_{k_1, k_2, \ldots} \frac{1}{k_1! k_2! \ldots} (g_1)^{k_1} (g_2)^{k_2} \ldots \]

\[ = \exp(g_1 + g_2 + \ldots) \]  

(3.87)
3.5 Lowest order terms

Since the perturbation $H_1$ contains interactions of different kinds, it is not meaningful to take just the first-order terms. Instead, the lowest order terms of each kind which does not vanish should be considered.

The first-order terms arising from the Coulomb interaction are:

The corresponding terms due to phonon exchange, which are of second-order in $H_1$, but first order in the phonon propagator, are:

Another diagram, first-order in the phonon propagator, arises from the second-order electron-phonon coupling:

The first-order term, arising from the lattice potential is:

The terms stemming from the Hartree and exchange-correlation potentials for the electrons are:

The pair potential gives rise to
The effective potentials, coupling to the phonons, lead to:

\[
H \xrightarrow{xc} H \quad H \xrightarrow{xc} H \quad H \xrightarrow{xc} H \quad H \xrightarrow{xc} H
\]

Finally there are the two constant terms:

\[
\begin{array}{c}
H \\
xc
\end{array}
\]

Most of the Hartree-type diagrams containing phonon propagators cancel each other:

\[
F \left[ \begin{array}{c}
\begin{array}{c}
\text{Diagram 1}
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{Diagram 2}
\end{array}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{Diagram 3}
\end{array}
\end{array}
\end{array} \right] = 0 \quad (3.89)
\]

\[
F \left[ \begin{array}{c}
\begin{array}{c}
\text{Diagram 4}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{Diagram 5}
\end{array}
\end{array}
\end{array} \right] = 0 \quad (3.90)
\]

\[
F \left[ \begin{array}{c}
\begin{array}{c}
\text{Diagram 6}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{Diagram 7}
\end{array}
\end{array}
\end{array} \right] = 0. \quad (3.91)
\]

Also

\[
F \left[ \begin{array}{c}
\begin{array}{c}
\text{Diagram 8}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{Diagram 9}
\end{array}
\end{array}
\end{array} \right] = 0. \quad (3.92)
\]

The term

\[
F \left[ \begin{array}{c}
\begin{array}{c}
\text{Diagram 10}
\end{array} + \begin{array}{c}
\begin{array}{c}
\text{Diagram 11}
\end{array}
\end{array}
\end{array} \right] = -\frac{1}{2} \int d^3r_1 \int d^3r_2 \frac{n(r_1)n(r_2)}{|r_1 - r_2|} \quad (3.93)
\]

cancels the Hartree energy which has to be subtracted from $\Delta \Omega$ in Eq. (3.5),
3.5. Lowest order terms

\[ F \left[ \begin{array}{c} \circ \rightarrow \text{xc} \end{array} \right] = - \int d^3r n(r) v_{\text{xc}}(r) \] (3.94)

cancels the exchange-correlation potential and

\[ F \left[ \begin{array}{c} \circ \rightarrow \text{ie} \end{array} \right] = - \int d^3r n(r)v_{\text{ie}}^i(r) = - \int \Gamma_{\text{ie}} \] (3.95)

is compensated up to harmonic order by \( \int \Gamma_{\text{ie}}^{(0,1,2)} \).

\[ F \left[ \begin{array}{c} \text{xc} + \text{xc} \end{array} \right] = - \frac{1}{2} \sum_{(\alpha,\iota)\neq(\alpha',\iota')} V_{\text{xc},\alpha,\alpha'}(R_{\alpha,\iota}, R_{\alpha',\iota'}) \right] - \sum_{\lambda\iota} V_{\text{xc},\lambda,\iota,\lambda',\iota'}^{(2)}(2n_{\beta}(\Omega_{\lambda\iota}) + 1) \] (3.96)

cancels the ionic correlation term \( \int \Gamma_{\text{ie}}^{(0,1,2)} \). Finally

\[ F \left[ \begin{array}{c} \text{xc} \end{array} + \text{xc} \end{array} \right] = \int d^3r \int d^3r' (\chi(r, r') \Delta_{\text{xc}}^*(r, r') + h.c) \] (3.97)

cancels the xc pair potential.

As already stated in section 2.4 about the KS phonons, we neglect the influence of superconductivity on the phonons, i.e., we neglect the dependence of the correlation potential acting on the ions on the superconducting order parameter. The functional constructed here will only serve for the calculation of the effective pair potential \( \Delta_{\text{xc}} \) and the effective interaction \( f_{\text{xc}} \) which are defined as functional derivatives of this energy functional with respect to the anomalous density. Neglecting the influence of superconductivity on the phonons, the term

\[ F \left[ \begin{array}{c} \text{xc} + \text{xc} \end{array} \right] = \sum_{\lambda\iota} \frac{V_{\text{xc},\lambda\iota}^2}{\Omega_{\lambda\iota}} \] (3.98)

does not depend on the anomalous density. Hence its functional derivative with respect to \( \chi \) is zero and the term can be omitted.

Up to harmonic order, the exchange-correlation free energy functional results in:

\[ F_{\text{xc}}[n, \chi, \Gamma] = F \left[ \begin{array}{c} \text{xc} \end{array} + \text{xc} \end{array} + \text{xc} \right] + \text{xc} \]
\[
\begin{align*}
\text{Chapter 3. Perturbation expansion for the xc terms}
\end{align*}
\]

\[=: F^{(A)}_{xc}[n, \chi, \Gamma] + F^{(B)}_{xc}[n, \chi, \Gamma] + F^{(C)}_{xc}[n, \chi, \Gamma] + F^{(D)}_{xc}[n, \chi, \Gamma] \]

\[= \int d^3r_1 \int d^3r_2 \frac{1}{|r_1 - r_2|} \left[ 1 - \frac{\epsilon_i - \mu}{E_i} \tanh(\frac{\beta}{2} E_i) \right] u(i,j) \left[ 1 - \frac{\epsilon_j - \mu}{E_j} \tanh(\frac{\beta}{2} E_j) \right] \]

\[-\frac{1}{4} \sum_{ij} \left( 1 - \frac{\epsilon_i - \mu}{E_i} \tanh(\frac{\beta}{2} E_i) \right) u(i,j) \left( 1 - \frac{\epsilon_j - \mu}{E_j} \tanh(\frac{\beta}{2} E_j) \right) \]

\[-\frac{1}{2} \sum_{ij} \int d\Omega \alpha^2 F_{ij}(\Omega) \frac{\Delta_i \Delta_j^*}{E_i E_j} (I(E_i, -E_j, \Omega) - I(E_i, E_j, \Omega)) \]

\[-\frac{1}{2} \sum_{ij} \int d\Omega \alpha^2 F_{ij}(\Omega) \left[ 1 + \frac{\epsilon_i - \mu}{E_i} \frac{\epsilon_j - \mu}{E_j} \right] I(E_i, E_j, \Omega) \]

\[+ \left( 1 - \frac{\epsilon_i - \mu}{E_i} \frac{\epsilon_j - \mu}{E_j} \right) I(E_i, -E_j, \Omega) \quad (3.99) \]

with

\[u(i,j) = \int d^3r \int d^3r' \frac{\varphi_i^*(r) \varphi_j(r') \varphi_i(r') \varphi_j^*(r)}{|r - r'|} \]

\[\alpha^2 F_{ij}(\Omega) = \sum_{\lambda q} |g_{ijq}|^2 \delta(\Omega - \Omega_{\lambda q}) \]

\[g_{ijq}^\lambda = \int d^3r \varphi_i^*(r) V_{\lambda q}(r) \varphi_j(r) \]

\[I(E_i, E_j, \Omega) = f_\beta(E_i) f_\beta(E_j) n_\beta(\Omega) \times \left( \frac{e^{\beta E_i} - e^{\beta(E_i + \Omega)}}{E_i - E_j - \Omega} - \frac{e^{\beta E_j} - e^{\beta(E_j + \Omega)}}{E_i - E_j + \Omega} \right) \]

The notation \(\alpha^2 F_{ij}(\Omega)\) is in analogy to Eliashberg theory. The terms \(F^{(C)}_{xc}\) and \(F^{(D)}_{xc}\) resemble the basic diagrams of Eliashberg theory [7]. One has to emphasize that, although the KS-BdG equations (2.73), (2.74) are purely static, the Eliashberg-type retardation effects are completely contained in the xc functional.

### 3.6 Random Phase Approximation

The term, arising from \(F^{(A)}_{xc}\) is expected to be strongly repulsive. In the actual material, however, the bare Coulomb interaction will be screened considerably. One way to take this screening into account is to perform a RPA calculation, i.e. a partial summation of the ring diagrams. A feasible approximation for the xc free energy can be obtained by replacing the bare Coulomb interaction in the diagrams

\[
\begin{array}{c}
\text{and}
\end{array}
\]
by a screened interaction \( w \), which is obtained from the Dyson equation

\[
\begin{align*}
\vdots = \vdots + \begin{array}{c}
\text{\vdots}
\end{array}
\end{align*}
\] (3.100)

\[
\begin{align*}
w(\omega; \mathbf{r}, \mathbf{r}') &= u(\mathbf{r}, \mathbf{r}') + \int d^3r_1 \int d^3r_2 u(\mathbf{r}, \mathbf{r}_1) \chi^0(\omega; \mathbf{r}_1, \mathbf{r}_2) w(\omega; \mathbf{r}_2, \mathbf{r}')
\end{align*}
\]

with the KS response function of the normal state, considered approximately in the zero-temperature limit:

\[
\begin{align*}
\chi^0(\omega; \mathbf{r}, \mathbf{r}') &= \lim_{\delta \to 0^+} \sum_{\sigma} \sum_{i} \sum_{j} \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_i(\mathbf{r}') \times \\
&\times \left\{ \frac{1}{\omega - \epsilon_j + \epsilon_i + i\delta} - \frac{1}{\omega + \epsilon_j - \epsilon_i - i\delta} \right\}
\end{align*}
\] (3.101)

The resulting energy diagrams are:

\[
\begin{align*}
\begin{array}{c}
\text{\vdots}
\end{array}
\end{align*}
\] and \[
\begin{align*}
\begin{array}{c}
\text{\vdots}
\end{array}
\end{align*}
\]

In principle, of course, the energy corresponding to a screened interaction has to be calculated by coupling-constant integration technique. Using the above expressions for the energy corresponds to neglecting the difference of the interacting and non-interacting kinetic energy functionals. We expect this to be a good approximation. Furthermore the screened interaction is approximated by its static limit:

\[
\begin{align*}
w(\omega; \mathbf{r}, \mathbf{r}') \approx w(0; \mathbf{r}, \mathbf{r}')
\end{align*}
\] (3.102)

This approximation might be more serious. Within these approximations the energy functionals take structurally the same form as \( F_{xc}^{(A)} \) and \( F_{xc}^{(B)} \):

\[
\begin{align*}
F_{xc}^{(A)} &= \int d^3r_1 \int d^3r_2 |\chi(\mathbf{r}_1, \mathbf{r}_2)|^2 w(0; \mathbf{r}, \mathbf{r}') \\
&= \frac{1}{4} \sum_{ij} \left( \frac{\Delta_i}{E_i} \tanh(\frac{\beta}{2} E_i) \right) w(i, j) \left( \frac{\Delta_j}{E_j} \tanh(\frac{\beta}{2} E_j) \right)
\end{align*}
\] (3.103)

\[
\begin{align*}
F_{xc}^{(B)} &= -\frac{1}{4} \sum_{ij} \left( 1 - \frac{\epsilon_i - \mu}{E_i} \tanh(\frac{\beta}{2} E_i) \right) w(i, j) \left( 1 - \frac{\epsilon_j - \mu}{E_j} \tanh(\frac{\beta}{2} E_j) \right)
\end{align*}
\] (3.104)

where

\[
\begin{align*}
w(i, j) := \int d^3r \int d^3r' \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}) w(0; \mathbf{r}, \mathbf{r}') \varphi_j^*(\mathbf{r}) \varphi_i(\mathbf{r}).
\end{align*}
\] (3.105)

\( F_{xc}^{(A)} \) and \( F_{xc}^{(B)} \) replace \( F_{xc}^{(A)} \) and \( F_{xc}^{(B)} \) in the xc free energy since the first-order terms are contained in these RPA terms.
3.7 Exchange-correlation potentials

The exchange-correlation potentials are defined as the functional derivatives of the xc free energy with respect to the densities. The potentials corresponding to the terms $F^{(A)}_{xc}$ and $F^{(A)}_{xc}$ can be evaluated directly since this part of $F_{xc}$ is known as an explicit functional of $\chi$.

$$
\Delta^{(A)}_{xc}(r, r') = -\frac{\chi(r, r')}{|r - r'|} \tag{3.106}
$$

$$
\Delta^{(A)}_{xc}(r, r') = -w(0; r, r') \chi(r, r') \tag{3.107}
$$

and thus

$$
\Delta^{(A)}_{xc,k} = -\sum_{k'} u(k, k') \chi_{k'}, \tag{3.108}
$$

$$
\Delta^{(A)}_{xc,k} = -\frac{1}{2} \sum_{k'} u(k, k') \tanh\left(\frac{\mu}{E_k} \right) \Delta_{kk'} \tag{3.109}
$$

The remaining terms are only known as implicit functionals of $\chi$, but as an explicit functional of the KS orbitals $\varphi_k(r)$, the KS single-particle energies $(\epsilon_k - \mu)$ and the pair potential $\Delta_k$:

$$
F_{xc} = F_{xc}[\varphi_k(r), (\epsilon_k - \mu), \Delta_k] \tag{3.110}
$$

In order to be able to perform the above functional derivatives, we approximate that the exchange-correlation potential does not depend on the anomalous density:

$$
v_{xc}[n, \chi, \Gamma] \approx v_{xc}[n, \chi \equiv 0, \Gamma]. \tag{3.111}
$$

This is equivalent to a truncation of the self-consistency loop (see figure 2.1) after the first iteration and can be justified with the argument of the different energy scales. Thus the KS orbitals and the KS single-particle energies $\epsilon_k$ do not depend on $\chi$. $F_{xc}$ is then a function of the chemical potential $\mu$ and a functional of (complex) the pair potential.

$$
F_{xc} \approx F_{xc}[\mu, \Delta] \tag{3.112}
$$

Since the pair potential $\Delta_k$ is a complex function we will treat its modulus square $|\Delta_k|^2$ and its phase $\delta_k = \Delta_k/|\Delta_k|$ as independent quantities. The exchange-correlation pair potential can now be calculated by applying the chain-rule of functional derivatives. This is the appropriate treatment because most of the terms to be calculated depend only on the modulus square $|\Delta_k|^2$.

$$
\Delta_{xc,k} := -\frac{\delta F_{xc}[\mu, |\Delta|^2, \delta]}{\delta \chi_k^*} \tag{3.113}
$$
3.7. Exchange-correlation potentials

\[ F_{\text{xc}}[\mu, |\Delta|^2, \delta] = F_{\text{xc}}[\mu, |\Delta|^2, \delta] \bigg|_{p} \frac{\delta \mu}{\delta \chi^*_{k'}} \bigg| \sum_{k'} \left( \frac{\delta F_{\text{xc}}[\mu, |\Delta|^2, \delta]}{\delta |\Delta'|^2} \bigg|_{p} \frac{\delta |\Delta'|^2}{\delta \chi^*_{k'}} \right) \]

\[ - \sum_{k'} \left( \frac{\delta F_{\text{xc}}[\mu, |\Delta|^2, \delta]}{\delta (\delta_{k'})} \bigg| \frac{\delta (\delta_{k'})}{\delta \chi^*_{k'}} \right) \cdotp (3.113) \]

To determine the functional derivatives of \( \mu, |\Delta'|^2 \) and \( \delta_k \) with respect to \( \chi^* \), we remember that the particle density \( n(r) \) and the anomalous density \( \chi(r, r') \) are independent variables:

\[ \frac{\delta n(x)}{\delta \chi^*(r, r')} = 0 \quad (3.114) \]

and hence

\[ \frac{\delta n(x)}{\delta \chi^*_{k'}} = 0. \quad (3.115) \]

This also holds for the particle number

\[ N = \int d^3r \ n(r) \quad (3.116) \]

which is given as an explicit functional of \( \mu \) and \( \Delta \):

\[ N = \sum_k \left( 1 - \frac{\epsilon_k - \mu}{E_k} \tanh\left( \frac{\beta}{2} E_k \right) \right) \quad (3.117) \]

where the \( E_k \) are defined in Eq. (2.93). Applying the chain-rule to this derivative, one finds:

\[ 0 = \frac{\delta N[\mu, |\Delta|^2]}{\delta \mu} \bigg|_{p} \frac{\delta \mu}{\delta \chi^*_{k'}} + \sum_{k'} \left( \frac{\delta N[\mu, |\Delta|^2]}{\delta |\Delta'|^2} \bigg|_{p} \frac{\delta |\Delta'|^2}{\delta \chi^*_{k'}} \right) \cdotp (3.118) \]

Evaluation of the partial derivatives yields:

\[ 0 = \left( \sum_{k'} \frac{y_2(k')}{R_{k'}^2} \right) \left( \frac{\delta \mu}{\delta \chi^*_{k'}} \right) + \sum_{k'} \frac{y_1(k')}{2R_{k'}^2} \left( \frac{\delta |\Delta'|^2}{\delta \chi^*_{k'}} \right) \cdotp (3.119) \]

Here the definitions

\[ y_0(k) = \left( \frac{(\epsilon_k - \mu)^2}{E_k} \tanh\left( \frac{\beta}{2} E_k \right) + \frac{\beta |\Delta|^2}{\cosh\left( \frac{\beta}{2} E_k \right)^2} \right) \]

\[ y_1(k) = \left( \frac{(\epsilon_k - \mu)}{E_k} \tanh\left( \frac{\beta}{2} E_k \right) - \frac{\beta (\epsilon_k - \mu)}{\cosh\left( \frac{\beta}{2} E_k \right)^2} \right) \]

\[ y_2(k) = \left( \frac{|\Delta|^2}{E_k} \tanh\left( \frac{\beta}{2} E_k \right) + \frac{\beta (\epsilon_k - \mu)^2}{\cosh\left( \frac{\beta}{2} E_k \right)^2} \right) \]

have been used. Two further equations, containing the desired derivatives, can be obtained by differentiating

\[ \chi_{k'}[\mu, \Delta] = \frac{1}{2} \frac{\Delta_{k'}}{E_{k'}} \tanh\left( \frac{\beta}{2} E_{k'} \right) \quad (3.123) \]
and its complex conjugate with respect to $\chi_k^*$. This leads to:

$$0 = y_1(k')|\Delta_{k'}|^2 \left( \frac{\delta \mu}{\delta \chi_k^*} \right) + \frac{y_0(k')}{2} \left( \frac{\delta |\Delta_{k'}|^2}{\delta \chi_k^*} \right) + i|\Delta_{k'}|^2 E_{k'} \tanh \left( \frac{\beta}{2} E_{k'} \right) \left( \frac{\delta (\delta_{k'})}{\delta \chi_k^*} \right),$$

(3.124)

$$2 \delta_{k,k'} E_{k'}^2 \Delta_{k'} = y_1(k')|\Delta_{k'}|^2 \left( \frac{\delta \mu}{\delta \chi_k^*} \right) + \frac{y_0(k')}{2} \left( \frac{\delta |\Delta_{k'}|^2}{\delta \chi_k^*} \right) - i|\Delta_{k'}|^2 E_{k'} \tanh \left( \frac{\beta}{2} E_{k'} \right) \left( \frac{\delta (\delta_{k'})}{\delta \chi_k^*} \right).$$

(3.125)

Solving Eqs. (3.119), (3.124) and (3.125) yields:

$$\frac{\delta |\Delta_{k'}|^2}{\delta \chi_k^*} = 2 \frac{E_{k'}^2 \Delta_{k'} \delta_{k,k'} - |\Delta_{k'}|^2 y_1(k') \left( \frac{\delta \mu}{\delta \chi_k^*} \right)}{y_0(k')},$$

(3.126)

$$\frac{\delta (\delta_{k'})}{\delta \chi_k^*} = i \delta_{k,k'} \frac{E_{k'}}{\Delta_k^* \tanh \left( \frac{\beta}{2} E_{k} \right)}$$

(3.127)

and

$$\frac{\delta \mu}{\delta \chi_k^*} = - \sum_{k'} Z_0(k')$$

(3.128)

with

$$Z_0(k) = \frac{E_k}{y_0(k)} \frac{\beta}{2} \tanh \left( \frac{\beta}{2} E_k \right) \cosh \left( \frac{\beta}{2} E_k \right)^2$$

(3.129)

$$Z_1(k) = \frac{y_1(k)}{y_0(k)} \Delta_k.$$

(3.130)

The xc pair potential is then obtained from:

$$\Delta_{xc} = \frac{Z_1(k)}{\sum_{k'} Z_0(k')} \left[ \frac{\delta F}{\delta \mu} \left|_p \right. - 2 \sum_{k'} y_1(k') |\Delta_{k'}|^2 \left( \frac{\delta F}{\delta |\Delta_{k'}|^2} \right) \right|_p + 2 \frac{E_{k'}^2 \Delta_{k'}}{y_0(k')} \delta \left( \frac{\delta F}{\delta |\Delta_{k'}|^2} \right) \left|_p \right. - i \frac{E_k}{\Delta_k^* \tanh \left( \frac{\beta}{2} E_k \right)} \delta \left( \frac{\delta F}{\delta (\delta_{k'})} \right) \left|_p \right. \right].$$

(3.131)

The potential corresponding to the second diagram was already evaluated in [17] and results in:

$$\Delta^{(B)}_{xc} = \frac{1}{2} Z_1(k) \left[ \sum_{k_2} u(k, k_2) \left( 1 - \frac{\epsilon_{k_2} - \mu}{E_{k_2}} \tanh \left( \frac{\beta}{2} E_{k_2} \right) \right) \right]$$

$$- \sum_{k_1, k_2} Z_0(k_1) u(k_1, k_2) \left( 1 - \frac{\epsilon_{k_1} - \mu}{E_{k_1}} \tanh \left( \frac{\beta}{2} E_{k_1} \right) \right).$$

(3.132)
The partial derivatives of the third term of $F_{xc}$ are:

\[ \frac{\delta F_{xc}^{(C)}}{\delta \mu} \bigg|_p = \sum_{ij} \int d\Omega \, \alpha^2 F_{ij}(\Omega) \frac{\Delta_i \Delta_j^*}{E_i E_j} \times \]
\[ \left[ \frac{E_i - \mu}{E_i^2} (I(E_i, E_j, \Omega) - I(E_i, -E_j, \Omega)) \right. \]
\[ \left. + \frac{E_i - \mu}{E_i} (I'(E_i, E_j, \Omega) - I'(E_i, -E_j, \Omega)) \right], \tag{3.134} \]

\[ \frac{\delta F_{xc}^{(C)}}{\delta |\Delta_k|^2} \bigg|_p = \frac{1}{4} \sum_l \int d\Omega \, \alpha^2 F_{kl}(\Omega) \frac{1}{E_k E_l} \times \]
\[ \left\{ \left[ \frac{\Delta_i^* \Delta_k^* + \Delta_l \Delta_j^*}{E_k^2} \right] (I(E_k, E_l, \Omega) - I(E_k, -E_l, \Omega)) \right. \]
\[ \left. + \frac{\Delta_i \Delta_j^* + \Delta_i^* \Delta_l}{E_k} (I'(E_k, E_l, \Omega) - I'(E_k, -E_l, \Omega)) \right\}, \tag{3.135} \]

and

\[ \frac{\delta F_{xc}^{(C)}}{\delta \delta k} \bigg|_p = -\frac{i}{2} \sum_l \int d\Omega \, \alpha^2 F_{kl}(\Omega) \frac{\Delta_k \Delta_j^* - \Delta_i \Delta_l}{E_k E_l} \times \]
\[ (I(E_k, E_l, \Omega) - I(E_k, -E_l, \Omega)) \tag{3.136} \]

where

\[ I'(E_i, E_j, \Omega) := \frac{\partial}{\partial E_i} I(E_i, E_j, \Omega). \tag{3.137} \]

Inserting these into (3.131) one finds:

\[ \Delta_{xc}^{(B)} = \frac{1}{2} Z_1(k) \sum_{k_2} w(k, k_2) \left[ \frac{1}{2} - \frac{\epsilon_{k_2} - \mu}{E_{k_2}} \tanh \left( \frac{\beta}{2} E_{k_2} \right) \right] \]
\[ - \sum_{k_1, k_2} Z_0(k_1) w(k_1, k_2) \left[ \frac{1}{2} - \frac{\epsilon_{k_2} - \mu}{E_{k_2}} \tanh \left( \frac{\beta}{2} E_{k_2} \right) \right] \frac{1}{\sum_{k_1} Z_0(k_1)}. \tag{3.133} \]
\[
\left[ \frac{\Delta_l \Delta_k^* - \Delta_l^* \Delta_k}{E_k} \tanh\left(\frac{\Delta_l}{2 E_k} \cosh^2\left(\frac{\Delta_l}{2 E_k}\right) \right) + 2 \frac{\Delta_l (\epsilon_k - \mu)^2}{\Delta_k E_k^2} \right] \times \left( I(E_k, E_l, \Omega) - I(E_k, -E_l, \Omega) \right) + \frac{\Delta_l \Delta_k^* + \Delta_l^* \Delta_k}{E_k} \left( I'(E_k, E_l, \Omega) - I'(E_k, -E_l, \Omega) \right). \quad (3.138)
\]

The partial derivatives of \( F^{(D)}_{xc} \) are:

\[
\frac{\delta F^{(D)}_{xc}}{\delta \mu} \bigg|_p = \sum_{ij} \int d\Omega \alpha^2 F_{ij}(\Omega) \left\{ \frac{|\Delta_i|^2}{E_i^3} \frac{\epsilon_j - \mu}{E_j} \left( I(E_i, E_j, \Omega) - I(E_i, -E_j, \Omega) \right) + \left( 1 + \frac{\epsilon_i - \mu \epsilon_j - \mu}{E_i} \right) \frac{\epsilon_i - \mu}{E_i} I'(E_i, E_j, \Omega) + \left( 1 - \frac{\epsilon_i - \mu \epsilon_j - \mu}{E_i} \right) \frac{\epsilon_i - \mu}{E_i} I'(E_i, -E_j, \Omega) \right\} \quad (3.139)
\]

and

\[
\frac{\delta F^{(D)}_{xc}}{\delta |\Delta_k|^2} \bigg|_p = \frac{1}{2} \sum_{ij} \int d\Omega \alpha^2 F_{kl}(\Omega) \left\{ \frac{\epsilon_k - \mu \epsilon_l - \mu}{E_k^3} \left( I(E_k, E_l, \Omega) - I(E_k, -E_l, \Omega) \right) + \left( 1 + \frac{\epsilon_k - \mu \epsilon_l - \mu}{E_k} \right) \frac{1}{E_k} I'(E_k, E_l, \Omega) - \left( 1 - \frac{\epsilon_k - \mu \epsilon_l - \mu}{E_k} \right) \frac{1}{E_k} I'(E_k, -E_l, \Omega) \right\}. \quad (3.140)
\]

It follows that

\[
\Delta^{(D)}_{xc,k} = \frac{Z_1(k)}{\sum_{k'} Z_0(k')} \sum_{ij} \int d\Omega \alpha^2 F_{ij}(\Omega) \left[ \frac{|\Delta_i|^2}{E_i^3} \frac{\epsilon_j - \mu}{E_j} \left( 1 - \frac{y_1(i)}{y_0(i)} (\epsilon_i - \mu) \right) \left( I(E_i, E_j, \Omega) - I(E_i, -E_j, \Omega) \right) + \left( 1 + \frac{\epsilon_i - \mu \epsilon_j - \mu}{E_i} \right) \frac{\epsilon_i - \mu}{E_i} \frac{y_1(i)}{y_0(i)} \frac{|\Delta_i|^2}{E_i} I'(E_i, E_j, \Omega) + \left( 1 - \frac{\epsilon_i - \mu \epsilon_j - \mu}{E_i} \right) \frac{\epsilon_i - \mu}{E_i} \frac{y_1(i)}{y_0(i)} \frac{|\Delta_i|^2}{E_i} I'(E_i, -E_j, \Omega) \right] \\
- \frac{E_k \Delta_k}{y_0(k)} \sum_{ij} \int d\Omega \alpha^2 F_{kl}(\Omega) \left[ \frac{\epsilon_k - \mu \epsilon_l - \mu}{E_k^3} \left( I(E_k, E_l, \Omega) - I(E_k, -E_l, \Omega) \right) - \left( 1 + \frac{\epsilon_k - \mu \epsilon_l - \mu}{E_k} \right) I'(E_k, E_l, \Omega) - \left( 1 - \frac{\epsilon_k - \mu \epsilon_l - \mu}{E_k} \right) I'(E_k, -E_l, \Omega) \right]. \quad (3.141)
\]
3.8 Effective interaction

The effective interaction, which enters the linearized gap equation can be obtained as the linear coefficient of $\Delta_{xc,k}$. The terms contributions to the effective interaction due to the first-order Coulomb terms are:

\[
\begin{align*}
\tilde{f}_{xc}^{(A)}(k, k') &= u(k, k') \\
\tilde{f}_{xc}^{(B)}(k, k') &= \frac{\delta_{k,k'}}{\tanh^2\left(\frac{\beta}{2}(\epsilon_k - \mu)\right)} \left( \tanh\left(\frac{\beta}{2}(\epsilon_k - \mu)\right) - \frac{\beta}{2}(\epsilon_k - \mu) \cosh^2\left(\frac{\beta}{2}(\epsilon_k - \mu)\right) \right) \\
&\times \left[ \sum_{k_1} u(k, k_1) \left( 1 - \tanh\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right) \right) \right] \\
&\quad - \sum_{k_1k_2} \frac{\delta_{k_1,k_2}}{\cosh^2\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right)} \left( 1 - \tanh\left(\frac{\beta}{2}(\epsilon_{k_2} - \mu)\right) \right) \\
&= \sum_{k_1} \frac{\delta_{k,k_1}u(k, k_1)}{\cosh^2\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right)} \left( 1 - \tanh\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right) \right) \\
&\quad - \\
&\quad - \sum_{k_1k_2} \frac{\delta_{k_1,k_2}}{\cosh^2\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right)} \left( 1 - \tanh\left(\frac{\beta}{2}(\epsilon_{k_2} - \mu)\right) \right).
\end{align*}
\]

Replacing the bare Coulomb interaction by the RPA-screened interaction leads to:

\[
\begin{align*}
\tilde{f}_{xc}^{(A)}(k, k') &= w(k, k') \\
\tilde{f}_{xc}^{(B)}(k, k') &= \frac{\delta_{k,k'}}{\tanh^2\left(\frac{\beta}{2}(\epsilon_k - \mu)\right)} \left( \tanh\left(\frac{\beta}{2}(\epsilon_k - \mu)\right) - \frac{\beta}{2}(\epsilon_k - \mu) \cosh^2\left(\frac{\beta}{2}(\epsilon_k - \mu)\right) \right) \\
&\times \left[ \sum_{k_1} w(k, k_1) \left( 1 - \tanh\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right) \right) \right] \\
&\quad - \sum_{k_1k_2} \frac{\delta_{k_1,k_2}}{\cosh^2\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right)} \left( 1 - \tanh\left(\frac{\beta}{2}(\epsilon_{k_2} - \mu)\right) \right) \\
&= \sum_{k_1} \frac{\delta_{k,k_1}w(k, k_1)}{\cosh^2\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right)} \left( 1 - \tanh\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right) \right) \\
&\quad - \\
&\quad - \sum_{k_1k_2} \frac{\delta_{k_1,k_2}}{\cosh^2\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right)} \left( 1 - \tanh\left(\frac{\beta}{2}(\epsilon_{k_2} - \mu)\right) \right).
\end{align*}
\]

The phonons give rise to:

\[
\begin{align*}
\tilde{f}_{xc}^{(C)}(k, k') &= -2 \int d\Omega \alpha^2 F_{kk'}(\Omega) \times \\
&\quad \times \frac{I((\epsilon_k - \mu), -(\epsilon_{k'} - \mu), \Omega) - I((\epsilon_k - \mu), (\epsilon_{k'} - \mu), \Omega)}{\tanh\left(\frac{\beta}{2}(\epsilon_k - \mu)\right) \tanh\left(\frac{\beta}{2}(\epsilon_{k'} - \mu)\right)} \\
\tilde{f}_{xc}^{(D)}(k, k') &= - \frac{4 \delta_{k,k'}}{\sum_{k_1} \cosh^2\left(\frac{\beta}{2}(\epsilon_{k_1} - \mu)\right)} \left( \frac{1}{\tanh\left(\frac{\beta}{2}(\epsilon_k - \mu)\right)} - \frac{\beta}{2}(\epsilon_k - \mu) \sinh^2\left(\frac{\beta}{2}(\epsilon_k - \mu)\right) \right) \\
&\quad \left( \sum_{ij} \int d\Omega \alpha^2 F_{ij}(\Omega) I'(\epsilon_i - \mu, \epsilon_j - \mu, \Omega) \right) \\
&\quad - \frac{2 \delta_{k,k'}}{\tanh^2\left(\frac{\beta}{2}(\epsilon_k - \mu)\right)} \sum_{i} \int d\Omega \alpha^2 F_{ik}(\Omega) \times \\
&\quad \left[ 2(\epsilon_k - \mu) I'((\epsilon_k - \mu), (\epsilon_i - \mu), \Omega) \\
&\quad - \left( I((\epsilon_k - \mu), (\epsilon_i - \mu), \Omega) - I((\epsilon_k - \mu), -(\epsilon_i - \mu), \Omega) \right) \right].
\end{align*}
\]
Chapter 4

The LMTO method

4.1 Introduction

The central aim of band-structure methods is to solve the single-particle Schrödinger (or KS) equation of a periodic, extended system:

$$\left( -\frac{\nabla^2}{2} + v(r) \right) \varphi_{nk}(r) = \epsilon_{nk} \varphi_{nk}(r). \quad (4.1)$$

The two major strategies to tackle this problem are:

- variational or basis-set methods:
  The wave functions are expanded in terms of a fixed set of basis functions. In this basis-set expansion, the problem of solving the Schrödinger equation is transformed into a simple matrix eigenvalue problem. For accurate solutions, normally a large number of basis functions is needed. An example is the plane-wave method.

- scattering methods, like, e.g., the KKR method:
  They use a geometrical approximation of the potential (muffin-tin geometry) and solve the Schrödinger equation exactly for this potential. These methods require a high computational effort since the secular problem is not linear in energy. Furthermore, since they are not variational it is not straightforward to include corrections to the geometrical approximations done.

The LMTO (Linear Muffin Tin Orbital method) [38, 39, 40, 41] is a hybrid method, which combines the advantages of both strategies, mentioned above. It is a variational method using basis sets derived by the KKR [42, 43] scattering method. This leads to very small basis sets. Similar to the KKR method, the potential is approximated by a “muffin tin” potential, i.e., it is spherically symmetric around the atomic sites and constant in the interstitial volume. A sketch of such a potential is shown in figure 4.1. The LMTO-basis functions will be constructed from solutions of the Schrödinger equation in the interstitial region, the envelope functions, which will then be augmented inside the atomic spheres by numerical solutions of the
4.2 The basis functions and the ASA-Hamiltonian

A set of envelope functions which are regular at infinity is defined by the solutions of

\[ (-\frac{\nabla^2}{2} + \kappa^2) K^0_\kappa(r) = 0 \]

(4.2)

The solutions which are regular at infinity and divergent at a given site \( \mathbf{R} \) are given by spherical harmonics\(^1\) and the spherical Hankel functions \( n_l(\kappa r) \)

\[ K^0_{R=L}(r) = n_l(\kappa|\mathbf{r} - \mathbf{R}|) i^l Y_L(\mathbf{r} - \mathbf{R}). \]

(4.3)

The complete set of functions \( K^0_{R=L}(r) \) for each \( \mathbf{R} \) and \( L \) will be denoted\(^2\) by \( |K^0(\kappa)\rangle \). The parameter \( \kappa \) is related to the kinetic energy in the interstitial volume.

At each atomic site, the tails of the envelope functions originating from other atomic sites are regular functions. Thus they can be expanded in terms of the solutions of Eq. (4.2), which are regular at zero and diverge at infinity.

\[ |K^0(\kappa)\rangle = |K^0(\kappa)\rangle - |J^0(\kappa)\rangle S^0(\kappa) + |K^0(\kappa)\rangle^i \]

(4.4)

\( S^0(\kappa) \) are the KKR-structure constants and the \( |J^0(\kappa)\rangle \) are defined in analogy to (4.3) with the spherical Bessel functions:

\[ J^0_{R=\mathbf{R}}(r) = j_l(\kappa|\mathbf{r} - \mathbf{R}|) i^l Y_L(\mathbf{r} - \mathbf{R}). \]

(4.5)

---

\(^1\) The label \( L \) abbreviates the angular momentum quantum numbers \( l \) and \( m \).

\(^2\) The kets \(|f\rangle^\infty \) denote functions which are defined in the whole space. \(|f\rangle \) are defined only within their atomic spheres and \(|f\rangle^i \) only in the interstitial.
Since these envelope functions will be augmented inside the atomic spheres anyway, it is not necessary that they are regular in the "tail"-spheres. By mixing in a certain amount of the irregular solutions, a set of more localized envelope-functions can be constructed \[44, 45, 46\]. If one looks at the analogy between Eq. (4.2) and a Poisson equation, this corresponds to the screening of the long-range potential of a point charge at the central position by putting screening charges at the neighboring sites. The regular solutions are replaced by:

\[
|J^0(\kappa)| \rightarrow |J^\alpha(\kappa)| = |J^0(\kappa)| - \alpha|K^0(\kappa)|. \tag{4.6}
\]

where \(\alpha\) is called the screening parameter. This leads to:

\[
|K^\alpha(\kappa)|^\infty = |K^0(\kappa)| - |J^\alpha(\kappa)|S^\alpha(\kappa) + |K^\alpha(\kappa)|^i
= |K^0(\kappa)|^\infty (1 + \alpha S^\alpha(\kappa)). \tag{4.7}
\]

The so-called screened structure constants can be obtained from:

\[
S^\alpha(\kappa) = S^0(\kappa) + S^0(\kappa)\alpha S^\alpha(\kappa) \tag{4.8}
\]

or

\[
S^\alpha(\kappa) = S^0(\kappa) (1 - \alpha S^0(\kappa))^{-1}. \tag{4.9}
\]

A set of energy-dependent basis functions \(\hat{x}(\kappa, \epsilon)\)^\infty or muffin-tin orbitals (MTO’s) is defined by replacing the heads of the envelope functions by the exact solutions of the Schrödinger equation inside the spheres, \(\Phi_{RL}(\epsilon, r)\), or, in short-hand notation \(|\phi(\epsilon)|\) and the regular solutions \(|J^\alpha(\kappa)|\).

\[
|K^0(\kappa)| \rightarrow |\hat{K}(\kappa)| := N^\alpha(\kappa, \epsilon)|\Phi(\epsilon)| + P^\alpha(\kappa, \epsilon)|J^\alpha(\kappa)|. \tag{4.10}
\]

To ensure a continuous and smooth matching, the coefficients have to be:

\[
N^\alpha(\kappa, \epsilon) = \frac{\{J^\alpha(\kappa), K(\kappa)\}}{\{J^\alpha(\kappa), \Phi(\epsilon)\}} \tag{4.11}
\]

\[
P^\alpha(\kappa, \epsilon) = \frac{\{\Phi(\epsilon), K(\kappa)\}}{\{\Phi(\epsilon), J^\alpha(\kappa)\}} \tag{4.12}
\]

where \(\{f, g\}\) denotes the Wronskian

\[
\{f, g\} = s^2 [f(s)g'(s) - f'(s)g(s)] \tag{4.13}
\]

with \(s\) being the muffin-tin radius of the atomic sphere.

\[
|\hat{x}(\kappa, \epsilon)|^\infty = |\Phi(\epsilon)|N^\alpha(\kappa, \epsilon) + |J^\alpha(\kappa)| \left[ P^\alpha(\kappa, \epsilon) - S^\alpha(\kappa) \right] + |K^\alpha(\kappa)|^i. \tag{4.14}
\]

For \(\epsilon = E\) and \(\kappa^2 = E - V_{mtz}\) these orbitals form an exact solution of the muffin-tin problem with the energy \(E\). \(V_{mtz}\) is the value of the constant potential in the
interstitial volume. The unphysical tails of the orbitals vanish. This is expressed by the KKR tail-cancellation equation:

\[ P^\alpha(\kappa, \epsilon) - S^\alpha(\kappa) = 0 \]  

In a linearized variational scheme this tail-cancellation will not be complete. Thus one needs to augment also the orbital tails \( |J^\alpha(\kappa)\rangle \). As will be seen later, a large part of the energy dependence can be treated by augmenting these tails with the radial functions \( |\Phi\rangle \) and their energy derivatives \( |\partial^\gamma\Phi\rangle \). The energy derivatives \( |\partial^\gamma\Phi\rangle \) are defined by:

\[ |\partial^\gamma\Phi(\epsilon)\rangle := \frac{\delta}{\delta \epsilon} |\Phi(\epsilon)\rangle. \]  

They form the so-called orthonormal representation\(^4\), since they are orthonormal to the radial functions \( |\Phi\rangle \):

\[ \langle \Phi | \partial^\gamma \Phi \rangle = 0. \]  

The tails \( |J^\alpha(\kappa)\rangle \) have to be augmented continuously and smoothly, which is again established by choosing the appropriate coefficients.

\[ |J^\alpha(\kappa)\rangle \rightarrow |\tilde{J}^\alpha(\kappa)\rangle = \left( |\partial^\gamma\Phi\rangle + \sigma^\alpha |\Phi\rangle \right) X^\alpha. \]  

From the Wronskian relations one obtains:

\[ \sigma^\alpha = -\frac{\{J^\alpha, \partial^\gamma \Phi\}}{\{J^\alpha, \Phi\}} \]  

\[ X^\alpha = \{ \Phi, J^\alpha \} = \frac{\{J^\alpha, K\}}{\{\Phi^\alpha, K\}} \]

with

\[ |\partial^\alpha \Phi\rangle = |\partial^\gamma \Phi\rangle + \sigma^\alpha(\kappa) |\Phi\rangle. \]

Renormalized by the factor \( N^\alpha(\kappa) \) the energy dependent MTO’s are:

\[ |\chi^\alpha(\epsilon)\rangle^\infty = \left( |\tilde{K}(\kappa)\rangle + |\tilde{J}^\alpha(\kappa)\rangle S^\alpha(\kappa) + |K^\alpha(\kappa)\rangle \right) \frac{1}{N^\alpha(\kappa)} \]

\[ = |\Phi(\epsilon)\rangle \frac{N^\alpha(\kappa, \epsilon)}{N^\alpha(\kappa)} + |\partial^\alpha \Phi(\kappa)\rangle \frac{w}{2} \frac{1}{N^\alpha(\kappa)} [S^\alpha(\kappa) - P^\alpha(\kappa, \epsilon)] \frac{1}{N^\alpha(\kappa)} \]

\[ + |K^\alpha(\kappa)\rangle \frac{1}{N^\alpha(\kappa)} \]

where \( w \) is the average sphere size.

\(^3\)omitting the energy argument means, that the linearization energies \( e_\epsilon \) are inserted.

\(^4\)denoted by the superscript \( \gamma \).
Chapter 4. The LMTO method

The linearized ($\varepsilon = \varepsilon_{\nu}, \kappa = 0$) MTO is then:

$$|\chi^{\alpha}\rangle^{\infty} = \left( |\tilde{K}\rangle + |\tilde{j}^{\alpha}\rangle S^{\alpha} + |K^{\alpha}\rangle \right) \frac{1}{N^{\alpha}}$$
$$= |\Phi\rangle + |\tilde{\Phi}^{\alpha}\rangle h^{\alpha} + |K^{\alpha}\rangle / N^{\alpha}.$$  

(4.24)  

(4.25)

In the ASA the atomic spheres are chosen to overlap with a space-filling volume. Thus, the interstitial volume vanishes, and the interstitial terms are neglected. Using

$$\langle \Phi^{\alpha}|\Phi^{\alpha}\rangle = 1$$  

(4.26)  

$$\langle \Phi^{\alpha}|\tilde{\Phi}^{\gamma}\rangle = 0$$  

(4.27)  

$$\langle \Phi^{\alpha}|\tilde{\Phi}^{\alpha}\rangle = o^{\alpha}$$  

(4.28)  

$$\langle \tilde{\Phi}^{\alpha}|\Phi^{\alpha}\rangle = p^{\alpha},$$  

(4.29)

the ASA the Overlap- and Hamiltonian-matrices can be evaluated:

$$\mathcal{O}_{ASA}^{\alpha} = \langle \chi^{\alpha}|\chi^{\alpha}\rangle$$  

$$= 1 + h^{\alpha\dagger}o^{\alpha} + o^{\alpha}h^{\alpha} + h^{\alpha\dagger}p^{\alpha}h^{\alpha}$$  

(4.30)

and

$$\mathcal{H}_{ASA}^{\alpha} = \langle \chi^{\alpha}| - \frac{\nabla^2}{2} + V_{mtz}|\chi^{\alpha}\rangle$$  

$$= h^{\alpha} + h^{\alpha\dagger}o^{\alpha}h^{\alpha} + \varepsilon_{\nu}\mathcal{O}_{ASA}^{\alpha}.$$  

(4.31)

All quantities appearing in these matrices can be expressed in terms of the Wronskians and form the so-called potential parameters.

The LMTO-ASA eigenvalue-problem is thus:

$$\mathcal{H}_{ASA}^{\alpha} U = E \mathcal{O}_{ASA}^{\alpha} U.$$  

(4.32)

4.3 Sketch of a calculation

A self-consistent LMTO calculation is usually started by choosing an initial density, normally a superposition of atomic densities. From this density the effective potential is calculated. Also, an initial set of $\varepsilon_{\nu}$’s is chosen. With the potential at hand, the Schrödinger equation in the atomic spheres can be integrated for the given $\varepsilon_{\nu}$’s, yielding the radial functions $|\Phi\rangle$ and $|\tilde{\Phi}\rangle$. From those, the potential parameters are determined, and the Hamilton and Overlap matrices are set up and diagonalized. With the eigenvectors, the new density can be constructed and the new $\varepsilon_{\nu}$’s are now set to the center of mass of occupied parts of the corresponding bands. Now, the next iteration can be started.
4.4 The wave functions

The Bloch wave functions $\varphi_{nk}(r)$ of the non-superconducting material in the LMTO-ASA method are represented as follows:

$$\varphi_{nk}(r) = \frac{1}{\sqrt{N}} \sum_{\tau L} u^n_{\tau L} \chi^k_{\tau L}(r)$$  \hspace{1cm} (4.33)

$$\chi^k_{\tau L}(r) = \sum_T \text{e}^{i k T} \chi_{\tau L}(r - \tau - T)$$ \hspace{1cm} (4.34)

$$\chi_{\tau L}(r - R) = \sum_{R',L'} \left\{ \phi_{\tau' L'}(r - R) \Pi_{R' L' R L} + \phi_{\tau' L'}(r - R) \Omega_{R' L' R L} \right\}.$$ \hspace{1cm} (4.35)

The Bloch wave functions as well as the LMTO’s $\chi^k_{\tau L}(r)$ are normalized to the volume $\mathcal{V}$:

$$\int_{\mathcal{V}} \text{d}^3r \left| \varphi_{nk}(r) \right|^2 = 1.$$ \hspace{1cm} (4.36)

In the thermodynamic limit this volume goes to infinity.

As can be seen by comparison with Eq. (4.24) the matrices $\Pi$ and $\Omega$ are given by:

$$\Pi = 1 + \alpha h^\alpha$$ \hspace{1cm} (4.37)

$$\Omega = h^\alpha$$ \hspace{1cm} (4.38)

The following conventions are used:

- $R, R', \ldots$ denote general positions in the atomic lattice, i.e. the Bravais lattice plus the basis,
- $T, T', \ldots$ denote lattice vectors of the Bravais lattice,
- $\tau, \tau', \ldots$ are the coordinates of the Atoms in one unit cell.

The $\chi^k_{\tau L}(r)$ are Bloch-periodic functions, i.e.

$$\chi^k_{\tau L}(r + R) = \text{e}^{i k R} \chi^k_{\tau L}(r).$$ \hspace{1cm} (4.39)

In the following we use

$$\tilde{\varphi}_{nk}(r) := \begin{cases} \sqrt{N} \varphi_{nk}(r) & \text{for } r \text{ in elementary cell} \\ 0 & \text{else} \end{cases}$$  \hspace{1cm} (4.40)

$$\tilde{\chi}^k_{\tau L}(r) := \begin{cases} \chi^k_{\tau L}(r) & \text{for } r \text{ in elementary cell} \\ 0 & \text{else} \end{cases}$$ \hspace{1cm} (4.41)

where $N$ is the number of unit cells in the volume $\mathcal{V}$:

$$\mathcal{V} = NV_0.$$ \hspace{1cm} (4.42)
The values for vectors outside the first elementary cell are then generated by the Bloch condition.

These functions can be expressed by the Bloch sums of the LMTO matrices

\[
\Pi_{\tau' L; \tau L}^k := \sum_T e^{ikR} \Pi_{\tau' L; \tau L + T L} \\
\Omega_{\tau' L; \tau L}^k := \sum_T e^{ikR} \Omega_{\tau' L; \tau L + T L}.
\]

(4.43)

(4.44)

The Bloch transformed of the basis functions are:

\[
\chi_{\tau L}^k(r) = \sum_{\tau' L'} \left\{ \phi_{\tau' L'}(r) \Pi_{\tau' L' L; \tau L}^k + \dot{\phi}_{\tau' L'}(r) \Omega_{\tau' L' L; \tau L}^k \right\}
\]

(4.45)

and the Bloch wave functions can be expressed as:

\[
\tilde{\varphi}_{nk}(r) = \sum_{\tau L} \chi_{\tau L}^k(r) u_{nk}^{\tau L}
\]

\[
= \sum_{\tau L} \sum_{\tau' L'} \left\{ \phi_{\tau' L'}(r) \Pi_{\tau' L' L; \tau L}^k + \dot{\phi}_{\tau' L'}(r) \Omega_{\tau' L' L; \tau L}^k \right\} u_{nk}^{\tau L}
\]

\[
= \sum_{\tau' L'} \left\{ \phi_{\tau' L'}(r) A_{\tau' L'}^{nk} + \dot{\phi}_{\tau' L'}(r) B_{\tau' L'}^{nk} \right\}
\]

(4.46)

with

\[
A_{\tau' L'}^{nk} := \sum_{\tau L} \Pi_{\tau' L' L; \tau L}^k u_{nk}^{\tau L}
\]

\[
B_{\tau' L'}^{nk} := \sum_{\tau L} \Omega_{\tau' L' L; \tau L}^k u_{nk}^{\tau L}.
\]

For convenience we define:

\[
U_{\tau L j}^{nk} := \begin{cases} A_{\tau L}^{nk} : j = 1 \\ B_{\tau L}^{nk} : j = 2 \end{cases} \quad \phi_{\tau L j}(r) := \begin{cases} \phi_{\tau L}(r) : j = 1 \\ \dot{\phi}_{\tau L}(r) : j = 2 \end{cases}.
\]

(4.47)

With these definitions the Bloch wave function reads:

\[
\tilde{\varphi}_{nk}(r) = \sum_{\tau L j} U_{\tau L j}^{nk} \phi_{\tau L j}(r).
\]

(4.48)
Chapter 5

The Coulomb interaction

5.1 LMTO-ASA representation

Our task is to calculate the Coulomb matrix elements

\[ u(nk, n'k') := \int d^3x \int d^3y \frac{\varphi_{nk}(x)\varphi_{nk}(y)\varphi_{n'k'}(y)\varphi_{n'k'}^*(x)}{|x - y|}, \]  

(5.1)

which are used for both the Coulomb term in the gap equation and the Coulomb term in the exchange-correlation terms. An approach to calculate this quantity within the LMTO-ASA band structure method, following to a large extent the lines of Svane and Andersen [47], will now be outlined.

Within the ASA the integration over all space is replaced by integrations over the atomic spheres accompanied by a summation over all sites:

\[ \int d^3r \to \sum_R \int_0^{R_{MT}} d^3(r - R). \]  

(5.2)

Using the Bloch relation and Eq. (4.40), i.e.

\[ \varphi_{nk}(r + R) = e^{i\mathbf{k}\cdot\mathbf{R}}\tilde{\varphi}_{nk}(r) \frac{1}{\sqrt{N}} \]  

(5.3)

we obtain:

\[ u(nk, n'k') = \frac{1}{N^2} \sum_{\tau_x, \tau_y} \sum_{T_x, T_y} e^{-i(k + k')(T_x - T_y)} \times \]

\[ \int d^3x \int d^3y \frac{\tilde{\varphi}_{nk}^*(x + \tau_x)\tilde{\varphi}_{nk}(y + \tau_y)\tilde{\varphi}_{n'k'}(y + \tau_y)\tilde{\varphi}_{n'k'}^*(x + \tau_x)}{|x + \tau_x + T_x - y - \tau_y - T_y|} \]

\[ = \frac{1}{N^2} \sum_{\tau_x, \tau_y} \sum_{T_x, T_y} e^{-i(k + k')(T_x - T_y)} \sum_{\tau_1, \tau_2, \tau_3, \tau_4} \sum_{j_1, j_2, j_3, j_4} \int d^3x \int d^3y \times \]

\[ \frac{\phi_{\tau_1L_1j_1}^*(x + \tau_x - \tau_1)\phi_{\tau_2L_2j_2}^*(y + \tau_y - \tau_2)\phi_{\tau_3L_3j_3}^*(y + \tau_y - \tau_3)\phi_{\tau_4L_4j_4}^*(x + \tau_x - \tau_4)}{|x + \tau_x + T_x - y - \tau_y - T_y|}. \]  

(5.4)
The summation indices \( \{ \tau, L, j \} \) are abbreviations for summations over \( \tau_1, \tau_2, \tau_3, \tau_4, \ldots \). The functions \( \phi_{\tau Lj}(r) \) vanish outside their sphere. Furthermore the overlap between neighboring sites is neglected within the ASA. Therefore an integration of the function \( \phi(r + R) \) over a sphere centered around the origin of \( r \) only contributes if \( R = 0 \). Thus we can write:

\[
\int d^3r \phi_{\tau Lj}(r + R) = \int d^3r \phi_{\tau Lj}(r) \delta_{R,0}.
\]

(5.5)

The matrix elements are then:

\[
u(nk, n'k') =
= \frac{1}{N^2} \sum_{\tau \tau' \{ L,j \}} e^{-i(k+k')(Tr_{\tau}-Tr_{\tau'})} \sum_{\{L,j\}} U_{\tau Lj}^{nk'} U_{\tau Lj}^{nk} U_{\tau' L'j'j} U_{\tau' L'j'j}^{n'k'} U_{n'k'}^{n} \times \]

\[
\int d^3x \int d^3y \frac{\phi_{\tau Lj1}(x) \phi_{\tau Lj2}(y) \phi_{\tau' L'j3}(y) \phi_{\tau' L'j4}(y)}{|x + \tau x + T x - y - \tau y - T y|} \]

\[
= \frac{1}{N^2} \sum_{\tau \tau' \{ L,j \}} \sum_{\{L,j\}} \{ U \} \sum_{T T'} e^{-i(k+k')T} \times \]

\[
\int d^3x \int d^3y \frac{\phi_{\tau' Lj1}(x) \phi_{\tau Lj2}(y) \phi_{\tau Lj3}(y) \phi_{\tau Lj4}(x)}{|x + \tau x + T - y - \tau y|} \]

\[
= \frac{1}{N} \sum_{\tau \tau' \{ L,j \}} \sum_{\{L,j\}} \{ U \} \sum_{T} e^{-i(k+k')T} I(\tau x, \tau y, \{ L, j \}, T).
\]

(5.6)

It is convenient to separate the on-site contribution, i.e. the \( \tau_x = \tau_y \) and \( T = 0 \) term, from the off-site contributions:

\[
u_{\text{on-site}}(nk, n'k') = \frac{1}{N} \sum_{\tau} \sum_{\{ L,j \}} \{ U \} I(\tau, \tau, \{ L,j \}, 0)
\]

(5.7)

\[
u_{\text{off-site}}(nk, n'k') = \frac{1}{N} \sum_{\tau \tau' \{ L,j \}} \sum_{\{L,j\}} \{ U \} \sum_{T} e^{-i(k+k')T} I(\tau x, \tau y, \{ L,j \}, T)
\]

(5.8)

where \( \sum' \) indicates that \( T = 0 \) has to be excluded for \( \tau_x = \tau_y \). We use the multipole expansion of the Coulomb interaction

\[
\frac{1}{|r - r'|} = \sum_{K} \frac{\delta^{K}_{r>}}{r^{K+1}} \frac{4\pi}{2K+1} Y_{K}(\hat{r}) Y_{K}(\hat{r'})
\]

(5.9)

and the expansion of the atomic functions

\[
\phi_{\tau Lj}(r) = \phi_{\tau Lj}(r) i^l Y_{lm}(\hat{r})
\]

(5.10)

where \( Y_{lm} \) are the complex spherical harmonics. The on-site integrals can readily be expressed as:

\[
I(\tau, \tau, \{ L,j \}, 0) = \sum_{K} \frac{4\pi}{2K+1} i^{-(l_1+l_4)} i^{l_2+l_3} \tilde{C}_{L1L4K} \tilde{C}_{L2L3K} \times
\]
\[
\int dx \int dy \sum_{j \geq 1} x \phi_{\tau_1 j_1}(x) x \phi_{\tau_2 j_2}(x) y \phi_{\tau_3 j_3}(y) y \phi_{\tau_4 j_4}(y).
\] (5.11)

\(\hat{C}\) are the \(\text{(modified) Gaunt coefficients:}\)

\[\hat{C}_{L_1 L_2 L_3} := \int d\Omega Y_{L_1}(\Omega) Y_{L_2}(\Omega) Y_{L_3}(\Omega).\] (5.12)

For the off-site contributions the above-mentioned expansion is used again.

\[\frac{1}{|x - (y - R)|} = \sum_K \frac{x^K}{|y - R|^{k+1}} \frac{4\pi}{2k+1} Y_K^*(\hat{x}) Y_K(y - R)\] (5.13)

\[= \frac{1}{w} \sum_K \frac{4\pi}{2k+1} \left(\frac{x}{w}\right)^k \left(\frac{w}{|y - R|}\right)^{k+1} (i^k Y_K(\hat{x}))^* i^k Y_K(y - R).\]

The spherical harmonics at center \(R\) can be expressed by those centered at the origin, using the unscreened KKR-ASA structure constants.

\[i^{k} \left(\frac{w}{|y - R|}\right)^{k+1} Y_K(\hat{y}) = - \sum_{K'} i^{k'} \left(\frac{y}{w}\right)^{k'} \frac{Y_{K'}(\hat{y})}{2(2k'+1)} S_{0K'RR}.\] (5.14)

Using the translational invariance of these structure constants, the Coulomb term can be written as:

\[\frac{1}{|x - (y - R)|} = - \frac{1}{w} \sum_{K,K'} \frac{2\pi}{(2k+1)(2k'+1)} \left(\frac{x}{w}\right)^k \left(\frac{y}{w}\right)^{k'} \times \]

\[\times i^{k'-k} Y_{K'}^*(\hat{y}) Y_{K'}(\hat{y}) S_{0K'RR}.\] (5.15)

The off-site integral is then:

\[\sum_T e^{-i(k + k')T} I_{\{\tau_x, \tau_y, \{L\}, T\}} = \]

\[- \frac{1}{w} \sum_{K,K'} \frac{2\pi}{(2k+1)(2k'+1)} i^{-(l_1 + l_4)} i^{(l_2 + l_3)} i^{(k'-k)} \times \]

\[\times \left(\int dx \left(\frac{x}{w}\right)^k x \phi_{\tau_1 j_1}(x) x \phi_{\tau_2 j_2}(x)\right) \left(\int dy \left(\frac{y}{w}\right)^{k'} y \phi_{\tau_3 j_3}(y) y \phi_{\tau_4 j_4}(y)\right) \times \]

\[\times \hat{C}_{L_1 L_2 L_3} \hat{C}_{L_2 L_3 K'} \left(\sum_T e^{-i(k + k')T} S_{0K'RR}.\right).\] (5.16)

The last parentheses defines exactly the Bloch transform of the structure constants. Taking all this together, the Coulomb matrix elements result in

\[u(nk, n'k') = \frac{1}{N} \sum_{\tau_x \tau_y \{L\}} \sum_{KK'} U_{\tau_x L_1 j_1} U_{\tau_y L_2 j_2} U_{\tau_y L_3 j_3} U_{\tau_y L_4 j_4} i^{-(l_1 + l_4)} i^{(l_2 + l_3)} \times \]

\[\times \hat{C}_{L_1 L_2 L_3} \hat{C}_{L_2 L_3 K'} \left(\sum_T e^{-i(k + k')T} S_{0K'RR}.\right).\]
\[ \times \tilde{C}^*_{L_1L_4K'} \tilde{C}^*_{L_2L_3K'} \left\{ \frac{\delta_{r_x,r_y} \delta_{K,K'}}{2k+1} \sigma^k_{r_z} \{ij\} \right\} \]

\[-\frac{1}{w} \frac{2\pi}{(2k+1)(2k'+1)} \right( k''-k \right) \rho^{k}_{r_{z_1}l_1l_{1}j_{1}j_{4}} \rho^{k'}_{r_{z_2}l_2l_{2}j_{3}j_{3}} S_{r_{z_1}K',r_{z_2}K}^{0,-(k+k')} \left\} \right. \]

\[ (5.17) \]

### 5.2 Product basis method

Another method to calculate the Coulomb matrix elements uses the product-basis set which was developed by F. Aryasetiawan and O. Gunnarson [48, 49, 50]. In Eq. (5.6) the Coulomb matrix elements are expressed in terms of matrix elements with respect to the radial functions \( \phi_{rL_j} \). It can be seen that the product functions

\[ \tilde{B}_{r_1}(r) = \phi_{r_1l_1j_1}(r) \phi_{r_2l_2j_2}(r) \]

form a complete set of basis functions for the calculation of the sought matrix elements. In order to accelerate the computation the basis set can be optimized by diagonalizing the overlap matrix and rejecting the functions with eigenvalues less than a certain threshold. Also the basis functions involving the energy derivatives \( \phi' \) are neglected here. This procedure yields the “optimized basis set” \( B_{r_{1}}(r) \) and its Fourier transform \( B_{q}(r) \). The calculation of the matrix elements

\[ u_{ij}(q) = \int d^3r \int d^3r' \frac{B^*_{iq}(r) B_{q}(r')}{|r-r'|} \]

is similar to the one, shown in the last section.

Starting from the the above expression, the matrix elements with respect to the Bloch representation can be obtained by:

\[ u(nk,n'k') = \sum_{ij} (A^*_{nk,n'k'})_{ij} \int d^3r \phi_{nk}(r) \phi_{nk}(r') B_{k+k'}(r) \]

where

\[ A_{nk,n'k'} = \int d^3r \phi_{nk}(r) \phi_{nk}(r') B_{k+k'}(r) \]

Also the matrix elements of the screened Coulomb interaction can be calculated by using the product-basis method. In this representation the Dyson equation (3.100) reads

\[ w_{ij}(\omega; q) = u_{ij}(q) + \sum_{kl} u_{ik}(q) \chi^0_{kl}(\omega; q) w_{ij}(\omega; q) \]

and can be solved by matrix inversion. The KS response function is calculated as:

\[ \chi^0_{ij}(q) = \sum_{\sigma} \sum_{k} \sum_{n} \sum_{n'} \sum_{\text{occ}} \sum_{\text{unocc}} (A^*_{i\sigma k,n'k'})(A_{j\sigma n'k'}^\dagger)^* \times\]

\[ \times \left\{ \frac{1}{\omega - \epsilon_{n'k+q} + \epsilon_{nk} + i\delta} - \frac{1}{\omega + \epsilon_{n'k+q} - \epsilon_{nk} - i\delta} \right\} \]

\[ (5.23) \]
5.2. Product basis method

with

\[ \tilde{A}^{nk,n'k'}_i = \int d^3 r \varphi_{nk}(r)\varphi^*_n(r)B_{ik-k'}(r). \] (5.24)

The Dyson equation can now be solved via matrix inversion:

\[ \tilde{w}(\omega; \mathbf{q}) = [1 - \hat{u}(\mathbf{q})\tilde{\chi}^0(\omega; \mathbf{q})]^{-1}\hat{u}(\mathbf{q}). \] (5.25)

The matrix elements \( w(k, k') \) can again be obtained by

\[ w(nk, n'k') = \sum_{ij} (A^{nk,n'k'}_i) w_{ij}(\omega = 0; k + k') (A^{nk,n'k'}_j)^*. \] (5.26)
Chapter 6

Results: Coulomb interaction

6.1 Aluminum

Aluminum is a typical BCS-type, i.e., phonon-mediated superconductor with a critical temperature of $T_c = 1.18 \, K$.\textsuperscript{1} The lattice structure of Aluminum is face-centered cubic. Figure 6.1 shows the Brillouin zone of an fcc structure and shows the positions of the symmetry points used in the following plots. The electronic structure of Aluminum is very well approximated by the free-electron gas. Figure 6.2 shows the band structure of Aluminum. For comparison, the band structure of the free-electron gas is shown in figure 6.3. The free-electron parabolas $\epsilon(k) = k^2/2$ are folded back into the first Brillouin zone of an fcc lattice with the same lattice constant as used in the Aluminum calculation. As can be seen in the plots, the lowest bands of Aluminum and the free-electron gas are in very good agreement. Due to the non-constant lattice potential of Aluminum, the degeneracies of the bands are

\textsuperscript{1}The value is taken from [51].
6.1. Aluminum

- Energy (Ry.)

**Figure 6.2**: Band structure of Aluminum, we calculated with the program LMTO-46 [52]. Here and in the following plots 'g' stands for T'.

**Figure 6.3**: Band structure of the free electron gas, folded back into the Brillouin zone of an fcc Bravais lattice.
removed, but the bands are still very close. Figure 6.4 shows the density of states for Aluminum and displays again that Aluminum is well described by the free-electron gas. From these results it can be expected that also the matrix elements of the Coulomb interaction show, at least for the lowest bands, a good concordance between the results for Aluminum and the results for the free-electron gas, which can be calculated analytically as:

$$u^{\text{free}}(\mathbf{k}, \mathbf{k}') = \frac{4\pi}{\mathcal{V}} \frac{1}{|\mathbf{k} + \mathbf{k}'|^2}.$$  \hspace{1cm} (6.1)

The results for the Coulomb matrix elements of Aluminum and the free-electron gas are shown in the figures 6.5 and 6.6. For the lowest band and $\mathbf{k} = \Gamma$ the plots coincide extremely well and demonstrate the precision of the methods, described in section 5. The increasing disagreement in figure 6.6 when $\mathbf{k}$ is shifted towards $\mathbf{k} = X$ can be explained as follows: Near the zone boundary the weak lattice potential of Aluminum has its strongest effect and leads to deviations from the free-electron results. This can be seen clearly in figure 6.2 by the splitting of the lowest bands between $X$ and $W$, which both lie on the zone boundary. This is also reflected in the wave functions and thus the Coulomb matrix elements of Aluminum differ from those of the free-electron gas.

Since the Fermi surface of Aluminum lies in the second and third band, the matrix elements of those bands have to be studied. The bands are usually simply numbered with increasing energy. At band crossings these labels do not correspond to the physical character of a band. As an example one can see in figure 6.7 that the
Figure 6.5: Comparison of Coulomb matrix elements $u(n = 1, k = \Gamma; n' = 1, k')$ of Aluminum along the line $k' = \{-X, \Gamma, X\}$: The solid curve is the free electron result, LMTO 1 refers to the product basis method and LMTO 2 to the direct LMTO expansion.

Figure 6.6: Comparison of Coulomb matrix elements $u(n = 1, k; n' = 1, k')$ of Aluminum along the line $-X, \Gamma, X$ where $k$ is shifted from $\Gamma$ towards $X$. 
second band at \( \mathbf{k} = X \) crosses three bands\(^2\) on its way to the \( \Gamma \)-point. Quantities such as, for instance, the Coulomb matrix elements show unphysical behavior like discontinuities if viewed just for one band labeled by numbering. To obtain smooth functions one has to follow the physical bands. Figure 6.8 and 6.9 show the bare and

![Graph showing band structure](image)

Figure 6.7: Details of the band structure of Aluminum.

the screened Coulomb matrix elements, \( u(n\mathbf{k}, n'\mathbf{k}') \) and \( w(n\mathbf{k}, n'\mathbf{k}') \), for the lowest bands. In figure 6.8 the first \( \mathbf{k} \)-vector is on the \( k_y \) axis near the center of the Brillouin zone in the third band. This band is degenerate with the second band. Thus the character of the wave functions of both bands are mixed. It can be seen that two bands exhibit the strong singularity in the bare Coulomb matrix elements and still a pronounced peak in the screened matrix elements. In figure 6.9 the first wave vector is also on the \( k_y \) axis but near the zone boundary and in the second band. At this point, the band is not degenerate. Only one peak near \( \mathbf{k} = -Y \) can be observed in the plots of the Coulomb matrix elements. Since \( \mathbf{k} \) is near the zone boundary, the peak extends to the opposite side of the Brillouin zone in the first band. In the extended zone scheme where the lines \( (-X, \Gamma, X) \), \( (-Y, \Gamma, Y) \), etc. are repeated periodically, one sees that these states are very close to each other in \( \mathbf{k} \)-space. In both figures can be seen that the bare Coulomb interaction between two Kohn-Sham particles is strongly repulsive, as was to be expected from free-electron calculations. This strong repulsive and divergent term, appearing in the gap equation, is likely to inhibit superconductivity, even in typical BCS-like superconductors like Aluminum. The effect of the phonons which will be discussed later, will not be strong enough to compensate the repulsion of the bare Coulomb interaction. This indicates, that

\(^2\)two of them are degenerate: near the \( X \)-point the bands denoted by the empty and filled squares coincide, near the \( \Gamma \)-point the bands denoted by \( x \)'s and asterisks coincide.
the first order treatment of the Coulomb interaction is not enough, even to describe conventional superconductors. The screened interaction, on the other hand, is much weaker and could easily be compensated by the phonon-mediated interaction. The results show that the RPA-like screening is sufficient to suppress this divergency. We can conclude that electronic correlations are essential to describe superconductivity.
Chapter 6. Results: Coulomb interaction

Figure 6.9: Results for the bare and the screened Coulomb interaction of Aluminum for $k = (0.1, 0.8, 0)$ and $n = 2$.

6.2 Niobium

Niobium is the elemental metal with the highest transition temperature, $T_c = 9.25K$.\(^3\) Its crystal structure is body-centered cubic. The Brillouin zone of the bcc structure is shown in figure 6.10 and displays the symmetry points. The band structure is given in figure 6.11. The flat bands near the Fermi level give rise to a very high density of states, shown in figure 6.12. To illustrate the band crossings and to relate the symbols to the band indices, figure 6.13 gives some details of the band structure on the lines on which the Coulomb matrix elements are studied.

\(^3\)The value is taken from [51].
6.2. Niobium

The results for the Coulomb interaction are plotted in the figures 6.14 to 6.17 for different band indices $n$ and wave vectors $k$.

The overall shape of the bare Coulomb interaction is similar to the Aluminum results: they show the strongly repulsive singularity for $k + k' = 0$. It can be noticed that the values for the screened interaction are in general lower in Niobium than in Aluminum. Furthermore their $k$ dependence is much weaker; the peak at $k + k' = 0$, coming from the long-range tail of the Coulomb interaction, nearly disappeared. This indicates that this long-range tail is much better screened in Niobium. An explanation therefore can be found in the density of state (see figure 6.12) which is much higher than in Aluminum. Hence more electrons near the Fermi surface are available for the screening. Therefore a high density of states at the Fermi level is favorable for a high transition temperature.
Chapter 6. Results: Coulomb interaction

Figure 6.12: Density of states for Niobium.

Figure 6.13: Details of the band structure of Niobium.
6.2. Niobium

Figure 6.14: Results for the bare and the screened Coulomb interaction of Niobium for \( \mathbf{k} = (0.1875, 0.1875, 0.125) \) and \( n = 2 \).
Figure 6.15: Results for the bare and the screened Coulomb interaction of Niobium for $k = (0.25, 0.25, 0.125)$ and $n = 3$. 
Figure 6.16: Results for the bare and the screened Coulomb interaction of Niobium for \( \mathbf{k} = (0.4375, 0.4375, 0.125) \) and \( n = 2 \).
Chapter 6. Results: Coulomb interaction

Figure 6.17: Results for the bare and the screened Coulomb interaction of Niobium for $\mathbf{k} = (0.4375, 0.4375, 0.125)$ and $n = 3$. 
Chapter 7

Results: phonon-mediated interaction

7.1 Material-independent properties

In conventional superconductors, superconductivity is caused by phonons. In BCS theory \[2\] the effective interaction is modeled by a square-well potential, which is attractive for energies within a shell of the width of the Debye frequency around the Fermi surface, and zero elsewhere. This simple model is justified by the Bardeen-Pines interaction \[6\], which can be obtained by applying a canonical transformation, valid to first order in the electron-phonon coupling, to an electron-phonon Hamiltonian. In the present theory, this phonon-mediated interaction is represented by the third and fourth term of the effective interaction \(f_{xc}(k, k')\). The dominant constituent is:

\[
f^{(C)}_{xc}(k, k') = -\int \! d\Omega \alpha^2 F_{k,k'}(\Omega) K(\epsilon_k - \mu, \epsilon_{k'} - \mu, \Omega) = -\sum_{k,k'} \sum_{\lambda q} |g_{kk'}^{\lambda q}|^2 K(\epsilon_k - \mu, \epsilon_{k'} - \mu, \Omega_{\lambda q}) \tag{7.1}
\]

with

\[
K(E, E', \Omega) := 2 I(E, -E', \Omega) - I(E, E', \Omega) \tanh(\frac{\beta E}{2}) \tanh(\frac{\beta E'}{2}) \tag{7.2}
\]

and

\[
I(E, E', \Omega) = f_\beta(E) f_\beta(E') n_\beta(\Omega) \left( \frac{e^{\beta E} - e^{\beta(E' + \Omega)}}{E - E' - \Omega} - \frac{e^{\beta E'} - e^{\beta(E + \Omega)}}{E - E' + \Omega} \right). \tag{7.3}
\]

The kernel \(K(\epsilon - \mu, \epsilon' - \mu, \Omega)\) is universal for all materials and determines how the material-specific electron-phonon coupling constants and phonon frequencies influence the transition temperature. Figure 7.1 shows a typical shape of this kernel as a function of the two energies. For low temperatures it has a sharp peak when both energies are near the Fermi energy. This is exactly the behavior one expects from the simple argument of BCS. At higher temperatures this peak is broadened.
Chapter 7. Results: phonon-mediated interaction

Figure 7.1: Kernel $K(\epsilon - \mu, \epsilon' - \mu, \Omega)$ for $T = 1\, \text{K}$ and $\Omega = 5\, \text{THz}$.

Figure 7.2: Kernel $K(\epsilon - \mu, \epsilon' - \mu, \Omega)$ for $T = 10\, \text{K}$ and $\Omega = 5\, \text{THz}$. 
7.1. Material-independent properties

In the figures 7.3 and 7.4 the dependence on the phonon frequency is displayed. This demonstrates that the soft phonons have a much stronger effect than high frequency phonons. Materials with soft phonons will thus have the tendency to show higher transition temperatures. Figures 7.5 and 7.6 depict the temperature dependence of $K(\epsilon - \mu, \epsilon' - \mu, \Omega)$. With increasing temperature the function is becoming broader and the peak value is decreasing.
Chapter 7. Results: phonon-mediated interaction

Figure 7.5: Kernel $K(\epsilon - \mu, \epsilon' - \mu, \Omega)$ as function of $T$ for $\epsilon' = \mu$ and $\Omega = 1$ THz.

Figure 7.6: Kernel $K(\epsilon - \mu, \epsilon' - \mu, \Omega)$ as function of $T$ for $\epsilon' = \mu$ and $\Omega = 5$ THz.
7.2 Simple metals

The linearized gap equation, derived in section 2.6 reads:

$$\Delta_k = -\frac{1}{2} \sum_{k'} f_{xc}(k, k') \frac{\tanh\left(\frac{\beta}{2}(\epsilon_{k'} - \mu)\right)}{\epsilon_{k'} - \mu} \Delta_{k'}$$  \hspace{1cm} (7.4)

As seen in chapter 3.8 the screened Coulomb interaction is given by:

$$f_{xc}^{(A)}(k, k') = w(k, k').$$  \hspace{1cm} (7.5)

Since the term $f_{xc}^{(B)}(k, k')$ vanishes on the Fermi surface its contribution in the gap equation will be small and for a first estimate we approximate:

$$f_{xc}^{(B)}(k, k') \approx 0.$$  \hspace{1cm} (7.6)

Thus we assume, that also for the phonon mediated interaction the term containing the anomalous Greens function is the dominant one. For a first approximative solution of the linearized gap equation $f_{xc}^{D}(k, k')$ will therefore be neglected. The gap equation then reads:

$$\Delta_k = -\frac{1}{2} \sum_{k'} \left[ w(k, k') - \int \frac{\omega^2 F_{kk'}(\omega) K(\epsilon_k - \mu, \epsilon_{k'} - \mu, \omega)}{\frac{\beta}{2}(\epsilon_{k'} - \mu)} \right] \frac{\tanh\left(\frac{\beta}{2}(\epsilon_{k'} - \mu)\right)}{\epsilon_{k'} - \mu} \Delta_{k'}$$  \hspace{1cm} (7.7)

where

$$K(\epsilon_k - \mu, \epsilon_{k'} - \mu, \omega) := \frac{I((\epsilon_k - \mu), -(\epsilon_{k'} - \mu), \omega) - I((\epsilon_k - \mu), (\epsilon_{k'} - \mu), \omega)}{\tanh(\frac{\beta}{2}(\epsilon_k - \mu)) \tanh(\frac{\beta}{2}(\epsilon_{k'} - \mu))}.$$  \hspace{1cm} (7.8)

In the simple metals, experiments have confirmed an s-wave order parameter. Hence the order parameter as well as the pair potential depends not on the direction of the $k$ vector at the Fermi surface. This allows us to write:

$$\Delta_k = \Delta(\epsilon_k).$$  \hspace{1cm} (7.9)

Introducing the unity

$$1 = \int d\epsilon' \delta(\epsilon' - \epsilon_{k'})$$  \hspace{1cm} (7.10)

on the right-hand side of the equation, and multiplying the whole equation by the density of states

$$\sum_k \delta(\epsilon - \epsilon_k) = N(\epsilon)$$  \hspace{1cm} (7.11)

one obtains:

$$\Delta(\epsilon) = -\frac{1}{2} \int d\epsilon' \left[ w^{CMB}(\epsilon, \epsilon') + w^{ph}(\epsilon, \epsilon') \right] \frac{\tanh\left(\frac{\beta}{2}(\epsilon' - \mu)\right)}{\epsilon' - \mu} \Delta(\epsilon')$$  \hspace{1cm} (7.12)
Chapter 7. Results: phonon-mediated interaction

\[ w^{ph}(\epsilon, \epsilon') = -\int d\Omega \alpha^2 \mathcal{F}(\epsilon, \epsilon', \Omega) K(\epsilon - \mu, \epsilon' - \mu, \Omega) \] (7.13)

\[ w^{Clb}(\epsilon, \epsilon') = \frac{1}{N(\epsilon)} \sum_{kk'} w(k, k') \delta(\epsilon - \epsilon_k) \delta(\epsilon' - \epsilon_{k'}) \] (7.14)

and

\[ \alpha^2 \mathcal{F}(\epsilon, \epsilon', \Omega) = \frac{1}{N(\epsilon)} \sum_{kk'} \alpha^2 \mathcal{F}_{kk'}(\Omega) \delta(\epsilon - \epsilon_k) \delta(\epsilon' - \epsilon_{k'}) \]

\[ = \frac{1}{N(\epsilon)} \sum_{kk'} \sum_{\lambda q} |\theta_{kk'}^{\lambda q}|^2 \delta(\Omega - \Omega_{\lambda q}) \delta(\epsilon - \epsilon_k) \delta(\epsilon' - \epsilon_{k'}). \] (7.15)

The function \( \alpha^2 \mathcal{F}(\epsilon, \epsilon', \Omega) \), evaluated at the Fermi surface, i.e. \( \epsilon = \epsilon' = \epsilon_F \), is the spectral function, used in Eliashberg’s theory. Due to the strongly peaked structure of \( \tanh(\frac{\epsilon' - \mu}{\epsilon - \mu}) \) and \( K(\epsilon - \mu, \epsilon' - \mu, \Omega) \) both the density of states and the spectral function can be replaced by their values at the Fermi surface. In the following we will calculate the phononic contribution of the effective interaction for the metals Al and Nb. For the Eliashberg function \( \alpha^2 \mathcal{F}(\Omega) \) we will use the simple model:

\[ \alpha^2 \mathcal{F}(\Omega) \approx \sum_n a_n e^{-b_n(\Omega - \Omega_n)^2}. \] (7.16)

This model is fitted to the data given in [51]. Comparisons of the electron-phonon coupling constants

\[ \lambda = 2 \int \frac{d\Omega}{\Omega} \alpha^2 \mathcal{F}(\Omega) \] (7.17)

which result from the fit with those given in [51] are presented in the captions of the figures 7.7 and 7.8, showing the results of the fits to Aluminum and Niobium. It should be mentioned that this model is not intended to give high precision, but to serve as a first estimate. More accurate calculations can be done by directly using the results of the linear-response calculations for the electron-phonon coupling [53, 51].

The effective interactions resulting from this model, evaluated at the experimental transition temperature of the respective material, are depicted in figures 7.9, 7.10, 7.11 and 7.12. It can be seen that the peak value for Niobium is higher than that of Aluminum. This is due to the fact that \( \alpha^2 \mathcal{F}(\Omega) \) has more weight at the lower frequencies in Niobium. This is also reflected in the higher value of the coupling constant \( \lambda \). The broadening of the peak for Niobium in comparison to Aluminum is mainly caused by the higher temperature at which the effective interaction is evaluated in Niobium.
7.2. Simple metals

Figure 7.7: Fit for $\alpha^2 F(\Omega)$ of Aluminum. $\lambda_{\text{fit}} = 0.44$, $\lambda_{\text{calc}} = 0.44$

Figure 7.8: Fit for $\alpha^2 F(\Omega)$ of Niobium $\lambda_{\text{fit}} = 1.24$, $\lambda_{\text{calc}} = 1.26$
Figure 7.9: The effective phonon-mediated interaction of Aluminum, evaluated at the experimental transition temperature $T = 1.18\text{K}$.

Figure 7.10: Logarithmic plot of the effective phonon-mediated interaction of Aluminum, evaluated at the experimental transition temperature $T = 1.18\text{K}$. 
Figure 7.11: The effective phonon-mediated interaction of Niobium, evaluated at the experimental transition temperature $T = 9.25$K.

Figure 7.12: Logarithmic plot of the effective phonon-mediated interaction of Niobium, evaluated at the experimental transition temperature $T = 9.25$K.
Chapter 8

Conclusion

The main goal of this work was the development of an “ab initio” method for describing strong-coupling superconductors. The principal idea to achieve this was to combine the OGK formulation of DFT for superconductors with the DFT for multi-component systems. In this way a consistent description of the electron-ion system is achieved. In chapter 2 the foundations of this DFT were given by proving the Hohenberg-Kohn theorem and by deriving the corresponding Kohn-Sham equations. The latter describe a system of non-interacting but superconducting electrons subject to an effective potential and a system of ions which interact among each other through an effective two-body interaction. The KS equation describing the ionic system was expanded around the equilibrium positions of the ions, giving rise to collective excitations, the KS phonons. The electronic KS system was treated in analogy to the OGK formalism, leading to a set of KS-Bogoliubov-de Gennes equations. Since the energy gap of the superconductor is usually 2 or 3 orders of magnitude smaller than typical electronic energies like band widths, the KS-BdG equations could approximately be decoupled into a generalized gap equation and the ordinary, normal-state band-structure problem. In contrast to the BCS gap equation, this generalized gap equation also contains correlation effects. In the vicinity of the transition temperature, the gap equation was linearized, leading to an effective interaction. This effective interaction was the central point of interest in the remainder of this work. In the regime of the linearized gap equation it was also possible to derive an exact linearized gap equation on the basis of linear-response theory. This supplies a possibility of estimating the error caused by the decoupling approximation. Chapter 3 was devoted to an analytical construction of the exchange-correlation functional and the corresponding effective interaction. Many-body perturbation theory was used to derive a first-order energy functional. To this end the Feynman rules for the diagrammatic determination of the grand canonical potential have been generalized to the case of KS perturbation theory in a superconducting electron-phonon system. All diagrams of lowest order have been evaluated. It could be shown that most of the diagrams cancel each other in lowest order and that the xc free energy functional is basically determined by four
diagrams: the direct and exchange term of the Coulomb interaction and two energy diagrams which correspond to the self-energy diagrams, used in Eliashberg theory. The xc pair potential has been calculated by taking the functional derivative of the energy functional. Since the latter is not known as explicit functional of the densities, but rather as a functional of the conjugate potentials, an implicit functional derivative had to be performed. A further functional derivative yielded the effective interaction. It has to be emphasized that the phononic part of this interaction contains, as opposed to the Bardeen-Pines interaction, also retardation effects of the phonons. For the Coulomb interaction we also proposed an alternative approximation going beyond first order by using an RPA-screened interaction in the diagrams. Chapter 4 gave a brief introduction into the LMTO-ASA method, which was used to calculate the band structures and which also forms the basis of the calculation of the matrix elements of the Coulomb interaction, as outlined in chapter 5. Some results for Aluminum and Niobium were presented in chapter 6. The strongly repulsive character of the bare Coulomb results indicated that a first-order treatment of the Coulomb interaction is not sufficient to describe superconductivity. The results for the RPA-screened interaction showed that the screening of the Coulomb interaction is very important. The residual Coulomb repulsion is much weaker and can easily be outbalanced by the phonon-mediated interaction. This phonon-mediated interaction was discussed in chapter 7. A central result was here that soft phonons have a much stronger influence on superconductivity and in particular on the transition temperature than hard phonons. This is in good agreement with experimental findings. For simple metals the material-specific quantities could be reduced to the Eliashberg function $\alpha^2 F(\Omega)$. Using a simple parameterization for this function, we presented numerical results for Aluminum and Niobium.

Now we have all the necessary ingredients to tackle the next large project: the numerical solution of the gap equation. A topic of special interest is, of course, the application to high-temperature superconductors. We have the hope, that the explicit calculation of the effective interaction will allow us to gain some insight about the mechanism of superconductivity in these systems.
Appendix A

Exact properties of the pairing potential matrix-elements

In this appendix we will examine some exact properties of the matrix $\Delta_{k,k'}$, which can be derived by group theory. The proof given here is a generalization of that, given in [17], to include the possibility of non $s$-wave pairing. It will be shown that the matrix is diagonal with respect to all symmetry-related quantum numbers, i.e. $(k, p, m)$. The matrix elements, written in complete labeling, are:

\[
\Delta(\alpha, p, k, m; \alpha', p', k', m') = \int \! d^3r \int \! d^3r' \varphi_{\alpha k m}(r)^* \Delta(r, r') \varphi_{\alpha' k' m'}(r'). \quad (A.1)
\]

$\alpha$ is the principal quantum number, not related to symmetry properties. $k$ is the Bloch wave vector, $p$ labels the representation of the point group and $m$ denotes the partner within the representation. Since the pair potential is not necessarily invariant under all symmetry operations of the underlying lattice, e.g. $d_{x^2-y^2}$ pairing in a tetragonal system, we decompose the pair potential into terms, transforming according to the irreducible representations of the point group of the lattice:

\[
\Delta(r, r') = \sum_{P_N} \Delta^{P_N}(r, r') \quad (A.2)
\]

with

\[
\Delta^{P_N}(R^{-1}r, R^{-1}r') = \sum_{M} \Gamma_{NM}^{P}(R) \Delta^{P_M}(r, r'). \quad (A.3)
\]

In analogy to Eq. (A.1), the matrix elements of the components, transforming according to a single representation are:

\[
\Delta^{P_M}(\alpha, p, k, m; \alpha', p', k', m') = \int \! d^3r \int \! d^3r' \varphi_{\alpha k m}(r)^* \Delta^{P_M}(r, r') \varphi_{\alpha' k' m'}(r'). \quad (A.4)
\]
A.1 Translation

Under the assumption that superconductivity does not break the translational invariance of the underlying lattice, the pair potential is invariant under lattice translations:

\[ \Delta(r - T, r' - T) = \Delta(r, r'). \]  

(A.5)

Substituting \( r \) and \( r' \) by \( r - T \) and \( r' - T \) in (A.1) and using the Bloch theorem for the orbitals \( \varphi^p_{\alpha km}(r) \), one finds:

\[
\Delta(\alpha, p, k, m; \alpha', p', k', m') = \\
= \int d^3r \int d^3r' e^{i\mathbf{k} \cdot \mathbf{T}} \varphi^p_{\alpha km}(r) \Delta(r, r')^* \varphi^p_{\alpha' k' m'}(r') \\
= e^{i(k - k') \cdot T} \int d^3r \int d^3r' \varphi^p_{\alpha km}(r) \Delta(r, r')^* \varphi^p_{\alpha' k' m'}(r'). 
\]  

(A.6)

Summation over all translations yields:

\[
\sum_T \Delta(\alpha, p, k, m; \alpha', p', k', m') = \\
= \sum_T e^{i(k - k') \cdot T} \int d^3r \int d^3r' \varphi^p_{\alpha km}(r) \Delta(r, r')^* \varphi^p_{\alpha' k' m'}(r') \\
N \Delta(\alpha, p, k, m; \alpha', p', k', m') = \\
= N \delta_{k, k'} \int d^3r \int d^3r' \varphi^p_{\alpha km}(r) \Delta(r, r')^* \varphi^p_{\alpha' k' m'}(r'). 
\]  

(A.7)

Since one only considers wave vectors within the first Brillouin zone, one obtains diagonality with respect to the wave vectors:

\[ \Delta(\alpha, p, k, m; \alpha', p', k', m') = \delta_{k, k'} \Delta(\alpha, p, m; \alpha', p', m'; k). \]  

(A.8)

A.2 Rotation

To exploit the behavior under rotations we will first consider just one component of the above decomposition (A.2)

\[
\Delta^{PM}(\alpha, p, m; \alpha', p', m'; k) = \int d^3r \int d^3r' \varphi^p_{\alpha km}(r) \Delta^{PM}(r, r')^* \varphi^p_{\alpha' k' m'}(r'). 
\]  

(A.9)

Analogous to the translation we substitute \( r, r' \) by \( R^{-1} r, R^{-1} r' \) and use the transformation rule for the Bloch orbitals

\[
P(\{R\}) \varphi^p_{\alpha km}(r) = \sum_{n=1}^l \Gamma^p(R)_{nm} \varphi^p_{\alpha(R,k)n}(r),
\]  

(A.10)
where we split the rotation \( R \) into \( R = \tilde{R}_j R_i \) with \( R_i \) being an operation, defining the “star” of \( k \), and \( \tilde{R}_j \in G_o(k) \). \( \Gamma^p(\tilde{R}_j) \) is the representation matrix of the \( p \)-th irreducible representation of the little group \( G_o(k) \).

\[
\Delta^{PM}(\alpha, p, m; \alpha', p', m'; k) = \\
= \int d^3 r \int d^3 r' \quad \varphi_{\alpha km}^p(R^{-1}r)^* \Delta^{PM}(R^{-1}r, R^{-1}r') \varphi_{\alpha' km'}^{p'}(R^{-1}r) \\
= \int d^3 r \int d^3 r' \sum_{n m' t} \Gamma_{nm}(\tilde{R}_j)^* \hat{\Gamma}_{NM}^p(R) \Gamma_{n'm'}^{p'}(\tilde{R}_j) \times \\
\quad \varphi_{\alpha(R, k)n}^p(r)^* \Delta^{PN}(r, r') \varphi_{\alpha'(R, k)m'}^{p'}(r') \\
= \sum_{n m N N'} \Gamma_{nm}(\tilde{R}_j)^* \hat{\Gamma}_{NM}^p(R) \Gamma_{N'M'}^{p'}(\tilde{R}_j) \Delta^{PN}(\alpha, p, n; \alpha', p', n'; R_i k) \quad \text{(A.11)}
\]

It has to be noted, that \( \Gamma^p \) are representations of the little group \( G_o(k) \) while \( \hat{\Gamma}^p \) is a representation of the point group \( G_o \), which will in general be reducible with respect to \( G_o(k) \). Using again \( R = \tilde{R}_j R_i \) we obtain

\[
\Delta^{PM}(\alpha, p, m; \alpha', p', m'; k) = \sum_{n m N N'} \Gamma_{nm}(\tilde{R}_j)^* \hat{\Gamma}_{NM}^p(R) \Gamma_{N'M'}^{p'}(\tilde{R}_j) \times \\
\quad \times \hat{\Gamma}_{NM}^{p'}(R_i) \Delta^{PN}(\alpha, p, n; \alpha', p', n'; R_i k) \quad \text{(A.12)}
\]

The little group of \( k \), \( G_o(k) \), is defined by

\[
\tilde{R}_j^{-1} k \cong k \quad \forall \quad \tilde{R}_j \in G_o(k). \quad \text{(A.13)}
\]

Thus it is evident that

\[
\Delta^{PM}(\ldots, \tilde{R}_j^{-1}k) = \Delta^{PM}(\ldots, k) \quad \forall \quad \tilde{R}_j \in G_o(k). \quad \text{(A.14)}
\]

On the other hand, \( \Delta^{PM} \) transforms as

\[
\Delta^{PM}(\ldots, R^{-1}k) = \sum_{N} \Gamma_{NM}^p(R) \Delta^{PN}(\ldots, k) \quad \forall \quad R \in G_o. \quad \text{(A.15)}
\]

This transformation rule holds also for all wave vectors \( k \) and all symmetry operations \( R \in G_o \), and thus in particular for the operations \( \tilde{R}_j \in G_o(k) \subset G_o \). This results in the following equation:

\[
\Delta^{PM}(k) = \sum_{N} \Gamma_{NM}^p(\tilde{R}_j) \Delta^{PN}(k) \quad \forall \quad \tilde{R}_j \in G_o(k). \quad \text{(A.16)}
\]

This result, of course, is also valid for general \( k \)-points, where the equation is trivially fulfilled because \( G_o(k) = \{ E \} \). For points of higher symmetry and non-trivial little groups it means that \( \Delta^{PM} \) either is a “left eigenvector” of \( \Gamma_{NM}^p \) with eigenvalue 1, or that \( \Delta^{PM}(\ldots, k) = 0 \), which denotes a node of this component of the pairing
potential. We can now carry out the summation over $N$ in Eq. (A.12) and eliminate $\hat{\Gamma}_{N_{N'}}^{\mu}(\tilde{R}_j)$ by using Eq. (A.16).

\[
\Delta_{PM}(\alpha, p, m; \alpha', p', m'; k) = \sum_{n'n'} \sum_{N} \Gamma_{nm}^{p}(\tilde{R}_j) \ast \Gamma_{n'm'}^{p'}(\tilde{R}_j) \times \\
\times \hat{\Gamma}_{N_{N'}}^{\mu}(R_i) \Delta_{PN}(\alpha, p, n; \alpha', p', n'; R_i, k) \quad \mathrm{(A.17)}
\]

Summing over all operations $\tilde{R}_j \in \mathcal{G}_p(k)$ and using the orthonormality theorem of group theory, one obtains:

\[
\sum_{\tilde{R}_j} \Delta_{PM}(\alpha, p, m; \alpha', p', m'; k) = \sum_{\tilde{R}_j} \sum_{nn'} \sum_{N} \Gamma_{nm}^{p}(\tilde{R}_j) \ast \Gamma_{n'm'}^{p'}(\tilde{R}_j) \hat{\Gamma}_{N_{N'}}^{\mu}(R_i) \times \\
\times \Delta_{PN}(\alpha, p, n; \alpha', p', n'; R_i, k) \quad \mathrm{(A.18)}
\]

\[
g_{\alpha}(k) \Delta_{PM}(\alpha, p, m; \alpha', p', m'; k) = \sum_{n'n'} \sum_{N} g_{\alpha}(k) \delta_{p,p'} \delta_{m,m'} \delta_{n,n'} \times \\
\hat{\Gamma}_{N_{N'}}^{\mu}(R_i) \Delta_{PN}(\alpha, p, n; \alpha', p', n'; R_i, k) \quad \mathrm{(A.19)}
\]

It can be seen immediately that $\Delta_{PM}(\alpha, p, m; \alpha', p', m'; k) = 0$ for $p \neq p'$ or $m \neq m'$. Considering the diagonal elements, one sees that the right-hand side does not depend on $m$. Thus $\Delta_{PN}(\alpha, p, n; \alpha', p', n; k)$ does not depend on $n$ and the summations over $n$ and $n'$ can be carried out. The first summation is canceled by the Kronecker symbol $\delta_{nn'}$ and the second one yields the dimension of the representation $l_p$. The resulting equation is:

\[
\Delta_{PM}(\alpha, \alpha'; p; R_i^{-1}k) = \sum_{N} \hat{\Gamma}_{N_{N'}}^{\mu}(R_i) \Delta_{PN}(\alpha, \alpha'; p; k) \quad \mathrm{(A.20)}
\]

with

\[
\Delta_{PM}(\alpha, \alpha'; p; k) = \int d^3r \int d^3r' \varphi_{\alpha kn}^{p}(r) \ast \Delta_{PM}(r, r') \varphi_{\alpha' kn}^{p'}(r') \quad \mathrm{(A.21)}
\]

Since all components of the pairing potential are diagonal in the symmetry labels $k, p$ and are independent of the partner label $m$ this result also holds for the complete pairing potential, independent of the transformation behavior under the operations of the lattice.

### A.3 Particle Interchange

As seen before the pairing potential for a singlet superconductor must be even under exchange of the coordinates,

\[
\Delta_{s}(r, r') = \Delta_{s}(r', r) \quad \mathrm{(A.22)}
\]

Thus the matrix-elements must obey

\[
\Delta_{s}(\alpha, \alpha', p, k) = \Delta_{s}(\alpha', \alpha, \bar{p}, -k) 
\quad \mathrm{(A.23)}
\]
The representation $\bar{p}$ denotes the representation obtained by taking the complex conjugate of the representation $p$. For a detailed discussion when $p$ and $\bar{p}$ are equivalent see for instance Cornwell [54].

### A.4 Time-Reversal Symmetry

Time-reversal symmetry is reflected in the condition

$$\Delta_s(\alpha, \alpha', p, \mathbf{k}) = \Delta_s^*(\alpha, \alpha', \bar{p}, -\mathbf{k}).$$

(A.24)

If this condition is not fulfilled, time-reversal symmetry is broken.
Appendix B

Definition of the Green’s functions

The normal electronic real-space Green’s function is defined as [37]:

\[
G_{\sigma,\sigma'}(r, r') := -\langle T \hat{\Psi}_{\sigma}(r, \tau) \hat{\Psi}_{\sigma'}^\dagger(r', \tau') \rangle. \tag{B.1}
\]

The generalization to the superconducting state can be done in analogy to Gor’kov’s anomalous Green’s functions

\[
\tilde{F}_{\sigma,\sigma'}(r, r') := -\langle T \hat{\Psi}_{\sigma}(r, \tau) \hat{\Psi}_{\sigma'}(r', \tau') \rangle \tag{B.2}
\]

\[
\tilde{F}_{\sigma,\sigma'}^\dagger(r, r') := -\langle T \hat{\Psi}_{\sigma}^\dagger(r, \tau) \hat{\Psi}_{\sigma'}^\dagger(r', \tau') \rangle. \tag{B.3}
\]

In analogy to Nambu [11], we define the two-component field operators

\[
\hat{\Psi}_{\sigma}(r) = \begin{pmatrix} \hat{\Psi}_{\sigma}(r) \\ \hat{\Psi}_{\sigma}^\dagger(r) \end{pmatrix} \tag{B.4}
\]

and

\[
\hat{\Psi}_{\sigma}^\dagger(r) = \begin{pmatrix} \hat{\Psi}_{\sigma}(r) \\ \hat{\Psi}_{-\sigma}(r) \end{pmatrix} \tag{B.5}
\]

and the Nambu Green’s function

\[
\tilde{G}_{\sigma,\sigma'}(r, r') := -\langle T \hat{\Psi}_{\sigma}(r, \tau) \hat{\Psi}_{\sigma'}^\dagger(r', \tau') \rangle = \begin{pmatrix} G_{\sigma,\sigma'}(r, r') & \tilde{F}_{\sigma,\sigma'}(r, r') \\ \tilde{F}_{-\sigma,\sigma'}^\dagger(r, r') & G_{-\sigma,\sigma'}(r, r') \end{pmatrix}. \tag{B.6}
\]

with

\[
G_{\sigma,\sigma'}(r, r') := -\langle T \hat{\Psi}_{\sigma}^\dagger(r, \tau) \hat{\Psi}_{\sigma'}(r', \tau') \rangle = -G_{\sigma',\sigma}(r', r). \tag{B.7}
\]

The Green’s functions defined in this way correspond to those used in [17]. The equation of motion for these Green’s functions is given by:

\[
\int q^3 q_1 \left( \frac{\delta(r - r_1)}{\delta \phi_{q_1} + h_s(r_1)} \Delta_s(r_1) \frac{\Delta_s(r_1)}{\Delta_s^2(r, r_1)} \delta(r - r_1) \left( \frac{\partial}{\partial \phi} - h_s(r_1) \right) \right) \times
\]

87
\[ \Psi_\sigma(r) = \left( \begin{array}{c} \hat{\Psi}_\sigma(r) \\ \mathrm{sgn}(\sigma) \hat{\Psi}_{-\sigma}(r) \end{array} \right) \]  

(B.11)

and

\[ \Psi^\dagger_\sigma(r) = \left( \hat{\Psi}^\dagger_\sigma(r), \mathrm{sgn}(\sigma) \hat{\Psi}_{-\sigma}(r) \right) \]  

(B.12)

the Nambu Green’s function reads:

\[ \hat{G}_{\sigma,\sigma'}(r, r'; \tau) = -\left( T \Psi_\sigma(r, \tau) \Psi^\dagger_{\sigma'}(r', \tau') \right) \]  

(B.13)

where

\[ F_{\sigma,\sigma'}(r, r'; \tau) = \mathrm{sgn}(\sigma') \hat{F}_{\sigma,\sigma'}(r, r'; \tau) = -\mathrm{sgn}(\sigma')(T \hat{\Psi}_\sigma(r, \tau) \hat{\Psi}_{-\sigma'}(r', \tau')) \]  

(B.15)

\[ F^\dagger_{\sigma,\sigma'}(r, r'; \tau) = \mathrm{sgn}(\sigma) \hat{F}^\dagger_{\sigma,\sigma'}(r, r'; \tau) = -\mathrm{sgn}(\sigma)(T \hat{\Psi}^\dagger_{\sigma}(r, \tau) \hat{\Psi}_{-\sigma'}(r', \tau')). \]  

(B.16)

\[ G_{\sigma,\sigma'}(r, r'; \tau) = \mathrm{sgn}(\sigma) \mathrm{sgn}(\sigma') \hat{G}_{\sigma,\sigma'}(r, r'; \tau) \]  

(B.17)

The equation of motion for these Green’s functions then becomes:

\[ \int d^3 r_1 \left( \frac{\delta}{\delta \hat{\Psi}_\sigma(r_1)} \left( \frac{\partial}{\partial \tau} + h_s(r_1) \right) \hat{G}_{\sigma,\sigma'}(r_1, r'; \tau) \right) = -\delta_{\sigma,\sigma'} \delta(\tau - \tau') \delta(r - r') \left( \begin{array}{c} 1 \\ 0 \\ 0 \\ 1 \end{array} \right). \]  

(B.18)

The Green’s functions of the Kohn-Sham system can easily be calculated by applying the Bogoliubov-de Gennes transformation to the definitions of the Green’s functions (B.1), (B.15) and (B.16). This leads to expressions containing the contractions of the Bogolon operators \( \hat{\gamma} \) and \( \hat{\gamma}^\dagger \):

\[ \langle T \hat{\gamma}_i \hat{\gamma}^\dagger \rangle = 0 = \langle T \hat{\gamma}^\dagger \hat{\gamma}_i \rangle \]  

(B.19)

and

\[ \Gamma_{\sigma,\sigma'}(i; j; \tau - \tau') := \langle T \hat{\gamma}_i \sigma(\tau) \hat{\gamma}^\dagger_{j\sigma'}(\tau') \rangle \]  

(B.20)

\[ \Gamma_{\sigma,\sigma'}^\dagger(i; j; \tau - \tau') := \langle T \hat{\gamma}^\dagger_i \sigma(\tau) \hat{\gamma}_{j\sigma'}(\tau') \rangle \]  

(B.21)
Their Fourier transforms are:

\[ \Gamma_{\sigma,\sigma'}(i, j; \omega_n) = -\frac{\delta_{i,j} \delta_{\sigma,\sigma'}}{i\omega_n - E_i} \] (B.22)

\[ \Gamma^\dagger_{\sigma,\sigma'}(i, j; \omega_n) = -\frac{\delta_{i,j} \delta_{\sigma,\sigma'}}{i\omega_n + E_i} \] (B.23)

In terms of the \( \Gamma \)'s the Green’s functions read:

\[
G_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}') = -\sum_{ij} \left[ u_i(\mathbf{r}) u_j^*(\mathbf{r}') \Gamma_{\sigma,\sigma'}(i, j; \tau - \tau') + 
+ \text{sgn}(\sigma) \text{sgn}(\sigma') v^*_j(\mathbf{r}) v_i(\mathbf{r}') \Gamma^\dagger_{\sigma,\sigma'}(i, j; \tau - \tau') \right] \] (B.24)

\[
F_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}') = \text{sgn}(\sigma') \sum_{ij} \left[ \text{sgn}(\sigma') u_i(\mathbf{r}) u_j^*(\mathbf{r}') \Gamma_{\sigma',-\sigma'}(i, j; \tau - \tau') + 
+ \text{sgn}(\sigma) v^*_j(\mathbf{r}) u_i(\mathbf{r}') \Gamma^\dagger_{\sigma',-\sigma'}(i, j; \tau - \tau') \right] 
\] (B.25)

\[
F^\dagger_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}') = \text{sgn}(\sigma) \sum_{ij} \left[ \text{sgn}(\sigma') u_i^*(\mathbf{r}) v_j(\mathbf{r}') \Gamma^\dagger_{\sigma',-\sigma'}(i, j; \tau - \tau') + 
+ \text{sgn}(\sigma) v_i(\mathbf{r}) u_j^*(\mathbf{r}') \Gamma_{\sigma',-\sigma'}(i, j; \tau - \tau') \right] . \] (B.26)

Using Eqs. (B.22) and (B.23) the Fourier transforms are:

\[
G_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}'; \omega_n) = \delta_{\sigma,\sigma'} \sum_{i} \left[ \frac{u_i(\mathbf{r}) u_i^*(\mathbf{r}')}{i\omega_n - E_i} + \frac{v_i(\mathbf{r}) v_i^*(\mathbf{r}')}{i\omega_n + E_i} \right] \] (B.27)

\[
F_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}'; \omega_n) = \delta_{\sigma',-\sigma} \sum_{i} \left[ \frac{v_i^*(\mathbf{r}) u_i(\mathbf{r}')}{i\omega_n + E_i} - \frac{u_i(\mathbf{r}) v_i^*(\mathbf{r}')}{i\omega_n - E_i} \right] \] (B.28)

\[
F^\dagger_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}'; \omega_n) = \delta_{\sigma',-\sigma} \sum_{i} \left[ \frac{u_i^*(\mathbf{r}) v_i(\mathbf{r}')}{i\omega_n + E_i} - \frac{v_i(\mathbf{r}) u_i^*(\mathbf{r}')}{i\omega_n - E_i} \right] . \] (B.29)

The equal-time limits can be expressed as:

\[
G_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}'; \tau^+) = \lim_{\eta \to 0^+} \sum_n e^{i\omega_n \eta} G_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}'; \omega_n) \] (B.30)

and analogously for the anomalous Green’s functions. Using

\[
\lim_{\eta \to 0^+} \sum_n \frac{e^{i\omega_n \eta}}{i\omega_n - E} = f_{\beta}(E) \] (B.31)

and remembering the representation of the densities (2.75) and (2.76), one obtains:

\[
\sum_{\sigma} G_{\sigma,\sigma'}(\mathbf{r}, \mathbf{r}^+) = n(\mathbf{r}) \] (B.32)

\[
F_{\sigma_1,\sigma_2}(\mathbf{r}_1, \mathbf{r}_2; \tau^+) = \delta_{\sigma_1,\sigma_2} \chi(\mathbf{r}_1, \mathbf{r}_2) \] (B.33)

\[
F^\dagger_{\sigma_1,\sigma_2}(\mathbf{r}_1, \mathbf{r}_2; \tau^+) = \delta_{\sigma_1,\sigma_2} \chi^*(\mathbf{r}_1, \mathbf{r}_2) \] (B.34)
The equal-time limit of the phononic Green’s function can be evaluated in a similar way:

\[
D_{\lambda q}(\tau, \tau^+) = \lim_{\eta \to 0^+} \sum_{\nu} e^{i\omega\eta} D_{\lambda q}(\omega_{\nu})
\]  

with

\[
D_{\lambda q}(\omega_{\nu}) = \frac{1}{i\omega_{\nu} - \Omega_{\lambda q}} - \frac{1}{i\omega_{\nu} + \Omega_{\lambda q}}.
\]  

Using

\[
\lim_{\eta \to 0^+} \sum_{\nu} \frac{e^{i\omega_{\nu}\eta}}{i\omega_{\nu} - \Omega} = -n_\beta(\Omega)
\]

one finds

\[
D_{\lambda q}(\tau, \tau^+) = -(2n_\beta(\Omega_{\lambda q}) + 1).
\]
Appendix C

Prefactors from Wick’s theorem

In this appendix we will not prove Wick’s theorem. This can be done in analogy to Fetter and Walecka [36] with the field operators transformed to the Bogolon operators. In the following we derive the prefactor of each diagram stemming from the reordering of the field operators, leading to the order required in the perturbation expansion.

C.1 Diagrams without pair potentials

First consider all diagrams which only contain normal Green’s functions. As in ordinary perturbation theory, each diagram contains one or more closed Fermion loops, i.e. closed paths consisting only of Green’s functions. In the perturbation expansion a closed loop is defined by the set of field operators which belong either to the same vertex or are connected through a contraction. The perturbation operators can always be regrouped without a change of sign such that they are of the form

\[ \hat{\psi}^\dagger \hat{\psi} \hat{\psi}^\dagger \hat{\psi} \ldots \]  

(C.1)

Since either both or none of the operators of a vertex belong to a loop, the operators can be rearranged such that the loops are separated:

\[ \underbrace{\hat{\psi}^\dagger \hat{\psi} \hat{\psi}^\dagger \hat{\psi}} \ldots \underbrace{\hat{\psi}^\dagger \hat{\psi} \hat{\psi}^\dagger \hat{\psi}} \ldots \ldots \]  

(C.2)

As shown, for instance, in [37] each loop yields a factor \((-1)\) when it is expressed through the contractions

\[ \text{Tr} \left\{ \rho^0 \hat{\psi} \hat{\psi}^\dagger \right\}. \]  

(C.3)

A diagram containing only normal Green’s functions thus corresponds to

\[ (-1)^q (-G)(-G)(-G) \ldots \]  

(C.4)

where \(q\) is the number of closed Fermion loops in the diagram.
Each diagram, which contains anomalous Green’s functions can be constructed from a diagram containing only normal Green’s functions by successive application of the following change:

Consider a chain of Green’s functions starting at vertex $B$ and ending at $A$

\[ \begin{array}{cccccc}
A & 1 & \cdots & n & B \\
\end{array} \tag{C.5} \]

where the dotted line represents an arbitrary chain of (normal and anomalous) Green’s functions. We replace this chain by

\[ \begin{array}{cccccc}
A & 1 & \cdots & n & B \\
\end{array} \tag{C.6} \]

where in the dotted part of the chain all arrows of the Green’s functions are turned around. This corresponds to the replacements:

\[
\begin{align*}
G_{\sigma;\sigma'}(r; r'; \tau) & \to G_{\sigma';\sigma}(r'; r; \tau) \tag{C.7} \\
F_{\sigma;\sigma'}(r; r'\tau') & \to F_{\sigma;\sigma'}^\dagger(r; r'\tau') \tag{C.8} \\
F_{\sigma;\sigma'}^\dagger(r; r'\tau') & \to F_{\sigma;\sigma'}(r; r'\tau'). \tag{C.9}
\end{align*}
\]

The two Green’s functions, enclosing the dotted line, are replaced by

\[
\begin{align*}
G_{\sigma_1,\sigma_A}(r_{1\tau_1}; r_A, \tau_A) & \to F_{\sigma_1,\sigma_A}(r_{1\tau_1}; r_A, \tau_A) \tag{C.10} \\
G_{\sigma_B,\sigma_n}(r_{B\tau_B}; r_n, \tau_n) & \to F_{\sigma_B,\sigma_n}^\dagger(r_{B\tau_B}; r_n, \tau_n). \tag{C.11}
\end{align*}
\]

The expression of the perturbation series, corresponding to chain (C.5) is:

\[ \begin{array}{cccc}
\hat{\Psi}(A) & \hat{\Psi}^\dagger(1)\hat{\Psi}(1) & \cdots & \hat{\Psi}^\dagger(n)\hat{\Psi}(n) & \hat{\Psi}^\dagger(B) \\
\end{array} \tag{C.12} \]

The field operators can be assumed to be ordered according to the contractions, corresponding to the Green’s functions of (C.5). The changes from (C.5) to (C.6) are that at all vertices 1 to $n$ the incoming and outgoing legs are interchanged. In terms of the contractions this is:

\[ \begin{array}{cccc}
\hat{\Psi}(A) & \hat{\Psi}^\dagger(1)\hat{\Psi}(1) & \cdots & \hat{\Psi}^\dagger(n)\hat{\Psi}(n) & \hat{\Psi}^\dagger(B) \\
\end{array} \tag{C.13} \]

Now, the field operators of all vertices 1 to $n$ can be rearranged such that the structure of the contractions resembles (C.12). Since in each vertex two operators
are exchanged, one obtains a prefactor \((-1)^n\) where \(n\) is the number of internal vertices in the chain:

\[
(-1)^n \, \hat{\Psi}(A) \, \hat{\Psi}(1) \hat{\Psi}(1) \ldots \hat{\Psi}(n) \hat{\Psi}(n) \hat{\Psi}(B) \, .
\] (C.14)

The contractions between the vertices 1 and \(n\) in (C.6) result from the corresponding contractions in (C.5) by taking the adjoints of the involved field operators. In terms of Green’s functions this means that all anomalous Green’s functions of (C.5) become their adjoints (with the same arguments) in (C.6), and all normal Green’s functions acquire a minus sign and change their direction. Therefore:

\[
G_{\sigma,\sigma'}(r\tau; r', \tau') \rightarrow -G_{\sigma',\sigma}(r'\tau', r\tau)
\] (C.15)

\[
F_{\sigma,\sigma'}(r\tau; r', \tau') \rightarrow F^\dagger_{\sigma',\sigma}(r\tau; r'\tau')
\] (C.16)

\[
F^\dagger_{\sigma,\sigma'}(r\tau; r'\tau') \rightarrow F_{\sigma,\sigma'}(r\tau; r'\tau')
\] (C.17)

Thus one can write (C.12) as:

\[
(-1)^{n+p} \langle T\hat{\Psi}(A)\hat{\Psi}(1) \rangle \ldots \langle T\hat{\Psi}(n)\hat{\Psi}(B) \rangle = (-1)^{n+p} \text{sgn}(\sigma_1) \, F_{\sigma,\sigma_1}(r_A \tau_A; r_1 \tau_1) \ldots \text{sgn}(\sigma_n) \, F^\dagger_{\sigma,\sigma_n}(r_n \tau_n, r_B \tau_B)\]
(C.18)

where \(p\) is the number of normal Green’s functions between the vertices 1 and \(n\) and \(\ldots\) denotes the sequence of Green’s functions without the signs acquired through (C.15). The sequence 1 \(\rightarrow\) \(n\), considered here, has a left leg pointing towards the vertex and a right leg pointing away from its vertex. Thus it has the properties of a normal Green’s function. Hence, the number of anomalous Green’s functions must be even. This implies that \(n + p\) is odd. Furthermore it is diagonal in the spin variable, i.e., it is only finite for \(\sigma_1 = \sigma_n\). Since the anomalous Green’s function is off-diagonal with respect to the spin, it follows directly, that \(\text{sgn}(\sigma_1) \, \text{sgn}(\sigma_n) = 1\), and hence the overall prefactor is \(-1\). Thus a factor of \(-1\) has to be included for each pair of anomalous Green’s functions.

### C.2 Diagrams with pair potentials

The terms of the perturbation are:

\[
\hat{H}_{\Delta^*} = \int d^3r \int d^3r' \Delta^*_\chi(\mathbf{r}, \mathbf{r}') \hat{\Psi}_1^\dagger(\mathbf{r}) \hat{\Psi}_1^\downarrow(\mathbf{r}')
\]

\[
= \frac{1}{2} \sum_{\sigma,\sigma'} \int d^3r \int d^3r' \delta_{\sigma,\sigma'} \text{sgn}(\sigma) \Delta^*_\chi(\mathbf{r}, \mathbf{r}') \hat{\Psi}_\sigma(\mathbf{r}) \hat{\Psi}_{\sigma'}(\mathbf{r}')
\] (C.19)

\[
\hat{H}_\Delta = \int d^3r \int d^3r' \Delta_\chi(\mathbf{r}, \mathbf{r}') \hat{\Psi}_1^\uparrow(\mathbf{r'}) \hat{\Psi}_1^\downarrow(\mathbf{r})
\]

\[
= \frac{1}{2} \sum_{\sigma,\sigma'} \int d^3r \int d^3r' \delta_{\sigma,\sigma'} \text{sgn}(\sigma') \Delta_\chi(\mathbf{r}, \mathbf{r}') \hat{\Psi}_\sigma^\dagger(\mathbf{r}) \hat{\Psi}_{\sigma'}^\downarrow(\mathbf{r}')
\] (C.20)
Consider an expression of the perturbation expansion (3.44) which contains one pair potential,

\[ \ldots \sum_{\sigma,\sigma'} \int d^3 r \int d^3 r' \left[ \frac{1}{2} \delta_{\sigma,-\sigma'} \text{sgn}(\sigma) \Delta_{xc}^*(r, r') \right] \ldots \hat{\Psi}_{\sigma}(r) \hat{\Psi}_{\sigma'}(r') \ldots \]  

(C.21)

where all field operators are fully contracted. The sign of this term is completely determined by the number of permutations necessary to rearrange the field operators such that they form the Green’s functions. These permutations are not affected if we, formally, replace

\[ \delta_{\sigma,-\sigma'} \text{sgn}(\sigma) \Delta_{xc}^*(r, r') \]  

by

\[ w(r', r) \hat{\Psi}_{\sigma'}^\dagger(r') \hat{\Psi}_{\sigma}^\dagger(r) \]

because the new field operators, introduced here, are already contracted. This leads to the term

\[ \ldots \sum_{\sigma,\sigma'} \int d^3 r \int d^3 r' \frac{1}{2} w(r', r) \hat{\Psi}_{\sigma'}^\dagger(r') \hat{\Psi}_{\sigma}^\dagger(r) \ldots \hat{\Psi}_{\sigma}(r) \hat{\Psi}_{\sigma'}(r') \ldots . \]  

(C.22)

Since the sign of this expression, when expressed in terms of Green’s functions, is determined by the Feynman rules for diagrams without pair potentials, we can deduce the sign of the original term: With

\[ \hat{\Psi}_{\sigma'}^\dagger(r') \hat{\Psi}_{\sigma}^\dagger(r) = F_{\sigma}(r', r) \text{sgn}(\sigma) \]  

(C.23)

we find that \( \delta_{\sigma,-\sigma'} \Delta_{xc}^*(r, r') \) corresponds to \( w(r, r') F_{\sigma}(r, r') \). Diagrammatically this can be written as:

\[
\begin{array}{c}
\text{r, } \sigma \\
\hdashline
\hdashline
\hdashline
\hdashline
\hdashline
\end{array}
\]  

corresponds to

\[
\begin{array}{c}
\text{r', } \sigma' \\
\hdashline
\hdashline
\hdashline
\hdashline
\hdashline
\end{array}
\]  

(C.24)

and in complete analogy:

\[
\begin{array}{c}
\text{r, } \sigma \\
\hdashline
\hdashline
\hdashline
\hdashline
\hdashline
\end{array}
\]  

corresponds to

\[
\begin{array}{c}
\text{r', } \sigma' \\
\hdashline
\hdashline
\hdashline
\hdashline
\hdashline
\end{array}
\]  

(C.25)

In the case of more than one pair potential this formal replacement can be done for all pair potentials occurring in the expression. Hence follows, that diagrams which contain pair potentials carry the same sign as the corresponding diagrams in which each pair potential is, formally, replaced in the above manner by an interaction and an anomalous Green’s function. The Feynman rules can therefore be generalized to the case including pair potentials by stating that each pair potential line has to be counted as an anomalous Green’s function.
Appendix D

Evaluation of the first order diagrams

For the evaluation of the diagrams the following relations for the equal-time limits of the Green’s functions will be used:

\[
\sum_{\sigma} G_{\sigma,\sigma}(r_\tau, r_{\tau}^+) = n(r) \quad (D.1)
\]

\[
F_{\sigma_1,\sigma_2}(r_1, r_2^{\tau^+}) = \delta_{\sigma_1,-\sigma_2} \chi(r_1, r_2) \quad (D.2)
\]

\[
F_{\sigma_1,\sigma_2}^{\dagger}(r_1, r_2^{\tau^+}) = \delta_{\sigma_1,-\sigma_2} \chi^*(r_1, r_2) \quad (D.3)
\]

\[
D_{\lambda q}(\tau, \tau^+) = -(2n_\beta(\Omega_{\lambda q}) + 1) \quad (D.4)
\]

\[
F \left[ \begin{array}{c}
\includegraphics[scale=0.5]{diagram1.png}
\end{array} \right] =
\]

\[
= -\frac{1}{\beta} \int_0^\beta d\tau \int d^3r_1 \int d^3r_2 \sum_{\sigma_1 \sigma_2} \left( -G_{\sigma_1 \sigma_1}(r_1, r_1^{\tau^+}) \right) \times
\]

\[
\frac{1}{2|r_1 - r_2|} \left( -G_{\sigma_2 \sigma_2}(r_2, r_2^{\tau^+}) \right)
\]

\[
= \frac{1}{2} \int d^3r_1 \int d^3r_2 \sum_{\sigma_1 \sigma_2} \left( \frac{1}{\beta} \sum_n e^{i\omega_n \tau} G(r_1, r_1; \omega_n) \right) \times
\]

\[
\frac{1}{|r_1 - r_2|} \left( \frac{1}{\beta} \sum_m e^{i\omega_m \tau} G(r_2, r_2; \omega_m) \right)
\]

\[
= \frac{1}{2} \int d^3r_1 \int d^3r_2 \frac{n(r_1)n(r_2)}{|r_1 - r_2|} \quad (D.5)
\]

\[
F \left[ \begin{array}{c}
\includegraphics[scale=0.5]{diagram2.png}
\end{array} \right] =
\]

95
\[
= - \frac{1}{\beta} \frac{(-1)^{1+1}}{1!} \int_0^\beta d\tau \int d^3r_1 \int d^3r_2 \sum_{\sigma_1\sigma_2} (-G_{\sigma_1\sigma_2}(r_1\tau, r_2\tau^+)) \times \\
\times \frac{1}{2|r_1 - r_2|} (-G_{\sigma_2\sigma_1}(r_2\tau^+, r_1\tau)) \\
= \frac{1}{2} \int d^3r_1 \int d^3r_2 \sum_{\sigma_1\sigma_2} \left( \frac{1}{\beta} \sum_n e^{i\omega_n \eta} \delta_{\sigma_1\sigma_2} G(r_1, r_2; \omega_n) \right) \times \\
\times \frac{1}{|r_1 - r_2|} \left( \frac{1}{\beta} \sum_m e^{-i\omega_m \eta} \delta_{\sigma_1\sigma_2} G(r_2, r_1; \omega_m) \right) \\
\approx -\frac{1}{4} \sum_{ij} \left( 1 - \frac{\epsilon_i}{E_i} \tanh\left( \frac{\beta}{2} E_i \right) \right) w(i, j) \left( 1 - \frac{\epsilon_j}{E_j} \tanh\left( \frac{\beta}{2} E_j \right) \right) 
\]

\text{(D.6)}

In the last step the decoupling approximation has been used.

\[
F \begin{array}{c}
\includegraphics[scale=0.5]{diagram1.png}
\end{array} = 
\]

\[
= - \frac{1}{\beta} \frac{(-1)^{1+1+1}}{1!} \int_0^\beta d\tau_1 \int d^3r_1 \int d^3r_2 \sum_{\sigma_1\sigma_2} (-F_{\sigma_1\sigma_2}(r_1\tau, r_2\tau^+)) \times \\
\times \frac{1}{2|r_1 - r_2|} (-F_{\sigma_2\sigma_1}^+(r_2\tau^+, r_1\tau)) \\
= \int d^3r_1 \int d^3r_2 \frac{|\chi(r_1, r_2)|^2}{|r_1 - r_2|} 
\]

\text{(D.7)}

\[
F \begin{array}{c}
\includegraphics[scale=0.5]{diagram2.png}
\end{array} = 
\]

\[
= - \frac{1}{\beta} \frac{(-1)^{2+2}}{2!} \int_0^\beta d\tau_1 \int d^3r_1 \int d^3r_2 \sum_{\sigma_1\sigma_2} \sum_{\lambda_q} \left(-G_{\sigma_1\sigma_1}(r_1\tau, r_1\tau^+)\right) \times \\
\times V_{\lambda_q}(r_1) (-D_{\lambda_q}(\tau_1 - \tau_2)) V_{\lambda_q}(r_2) \left(-G_{\sigma_2\sigma_2}(r_2\tau^+, r_2\tau^+)\right) \\
= \frac{1}{\beta} \int_0^\beta d\tau_1 \int d^3r_1 \int d^3r_2 \sum_{\lambda_q} n(r_1) V_{\lambda_q}(r_1) V_{\lambda_q}(r_2) n(r_2) \times \\
\times \left( \frac{1}{\beta} \sum_{\nu} e^{i\omega_\nu (\tau_1 - \tau_2)} \frac{2\Omega_{\lambda_q}}{(i\omega_\nu)^2 - \Omega_{\lambda_q}^2} \right) \\
= \frac{1}{2} \int d^3r_1 \int d^3r_2 \sum_{\lambda_q} n(r_1) V_{\lambda_q}(r_1) V_{\lambda_q}(r_2) n(r_2) 
\]
\[
X \left( \sum_{\nu} \left( \frac{1}{\beta^2} \int_{0}^{\beta} d\tau_1 \int_{0}^{\beta} d\tau_2 e^{i\omega_{\nu}(\tau_1 - \tau_2)} \right) \frac{2\Omega_{\lambda q}}{(i\omega_{\nu})^2 - \Omega_{\lambda q}^2} \right)
= -\frac{1}{2} \int d^3 r_1 \int d^3 r_2 n(r_1) \sum_{\lambda q} \frac{2V_{\lambda q}(r_1)V_{\lambda q}(r_2)}{\Omega_{\lambda q}^2} n(r_2)
= -\int d^3 r_1 \int d^3 r_2 n(r_1) \sum_{\lambda} \frac{V_{\lambda 0}(r_1)V_{\lambda 0}(r_2)}{\Omega_{\lambda 0}} n(r_2)
\] (D.8)

\[
F \left( \begin{array}{c}
\end{array} \right)
= -\frac{1}{\beta} \frac{(-1)^{2+1}}{2!} \int_{0}^{\beta} d\tau_1 \int_{0}^{\beta} d\tau_2 \int d^3 r_1 \int d^3 r_2 \sum_{\sigma_1 \sigma_2 \lambda q} (-G_{\sigma_1 \sigma_2}(r_1 \tau_1, r_2 \tau_2)) \times
\times V_{\lambda q}(r_1) \left( -D_{\lambda q}(\tau_1 - \tau_2) \right) V_{\lambda q}(r_2) \left( -G_{\sigma_2 \sigma_1}(r_2 \tau_2, r_1 \tau_1) \right)
= -\frac{1}{\beta^2} \int_{0}^{\beta} d\tau_1 \int_{0}^{\beta} d\tau_2 \int d^3 r_1 \int d^3 r_2 \sum_{\sigma_1 \sigma_2 \lambda q} \left( \frac{1}{\beta} \sum_{n_1} e^{i\omega_{n_1}(\tau_1 - \tau_2)} \delta_{\sigma_1 \sigma_2} G(r_1, r_2; \omega_{n_1}) \right) \times
\times V_{\lambda q}(r_1) \left( \frac{1}{\beta} \sum_{\nu} e^{i\omega_{\nu}(\tau_1 - \tau_2)} \frac{2\Omega_{\lambda q}}{(i\omega_{\nu})^2 - \Omega_{\lambda q}^2} \right) V_{\lambda q}(r_2)
\times \left( \frac{1}{\beta} \sum_{n_2} e^{i\omega_{n_2}(\tau_1 - \tau_2)} \delta_{\sigma_1 \sigma_2} G(r_2, r_1; \omega_{n_2}) \right)
= -\frac{1}{\beta^2} \int d^3 r_1 \int d^3 r_2 \sum_{\lambda q, n_1, n_2 \nu} \left( \frac{1}{\beta^2} \int_{0}^{\beta} d\tau_1 \int_{0}^{\beta} d\tau_2 e^{i(\omega_{\nu} - (\omega_{n_1} - \omega_{n_2}))(\tau_1 - \tau_2)} \right) = \delta_{\omega_{\nu} - \omega_{n_1} - \omega_{n_2}}
\times V_{\lambda q}(r_1) V_{\lambda q}(r_2) G(r_1, r_2; \omega_{n_1}) G(r_2, r_1; \omega_{n_2}) \frac{2\Omega_{\lambda q}}{(i\omega_{\nu})^2 - \Omega_{\lambda q}^2}
= -\frac{1}{\beta^2} \int d^3 r_1 \int d^3 r_2 \sum_{\lambda q, n_1, n_2 \nu} V_{\lambda q}(r_1) V_{\lambda q}(r_2)
\times G(r_1, r_2; \omega_{n_1}) G(r_2, r_1; \omega_{n_2}) \frac{2\Omega_{\lambda q}}{(i\omega_{n_1} - i\omega_{n_2})^2 - \Omega_{\lambda q}^2}
= -\int d^3 r_1 \int d^3 r_2 \sum_{\lambda q} V_{\lambda q}(r_1) V_{\lambda q}(r_2) \sum_{ij}
\left\{ u_i(r_2) u_i(r_1) u_j(r_1) u_j(r_2) I(E_i, E_j, \Omega_{\lambda q})
+ u_i(r_2) u_i(r_1) v_j(r_1) v_j(r_2) I(E_i, -E_j, \Omega_{\lambda q})
+ v_i(r_2) u_i(r_1) u_j(r_1) u_j(r_2) I(-E_i, E_j, \Omega_{\lambda q})
+ v_i(r_2) u_i(r_1) v_j(r_1) v_j(r_2) I(-E_i, -E_j, \Omega_{\lambda q}) \right\}
\] (D.9)
with

\[ I(E_i, E_j, \Omega) = \frac{1}{\beta^2} \sum_{n_1 n_2} \frac{1}{i \omega_{n_1} - E_i} \frac{1}{i \omega_{n_2} - E_j} \frac{2\Omega}{(i \omega_{n_1} - i \omega_{n_2})^2 - \Omega^2} \]  

(D.10)

Using the decoupling approximation this expression can be further evaluated:

\[
F \left[ \begin{array}{c}
\end{array} \right] =
\]

\[
= - \sum_{\lambda q} \sum_{ij} |g_{ij}^{\lambda q}|^2 \left\{ \left( |u_i|^2 |u_j|^2 + |v_i|^2 |v_j|^2 \right) I(E_i, E_j, \Omega_{\lambda q}) 
+ (2 |u_i|^2 |v_j|^2) I(E_i, -E_j, \Omega_{\lambda q}) \right\}
\]

\[
= - \frac{1}{4} \sum_{\lambda q} \sum_{ij} |g_{ij}^{\lambda q}|^2 \left\{ \left[ \left( 1 + \frac{e_i - \mu}{E_i} \right) \left( 1 + \frac{e_j - \mu}{E_j} \right) + \left( 1 - \frac{e_i - \mu}{E_i} \right) \left( 1 - \frac{e_j - \mu}{E_j} \right) \right] I(E_i, E_j, \Omega_{\lambda q}) 
+ 2 \left[ \left( 1 + \frac{e_i - \mu}{E_i} \right) \left( 1 - \frac{e_j - \mu}{E_j} \right) \right] I(E_i, -E_j, \Omega_{\lambda q}) \right\} \quad \text{(D.11)}
\]

where

\[ g_{ij}^{\lambda q} := \int d^3 r \varphi_i^*(r) V_{\lambda q}(r) \varphi_j(r) \]  

(D.12)

and \( \varphi_i^*(r) = \varphi_i(r) \) and \( E_i = E_j \) was used.

\[
F \left[ \begin{array}{c}
\end{array} \right] =
\]

\[
= - \frac{1}{\beta} \frac{(-1)^{2+1+1}}{2!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int d^3 r_1 \int d^3 r_2 \sum_{\lambda q} \sum_{\sigma_1 \sigma_2} (-F_{\sigma_1 \sigma_2}(r_1 \tau_1, r_2 \tau_2)) \times 
\]

\[ V_{\lambda q}(r_1) (-D_{\lambda q}(\tau_1 - \tau_2)) V_{\lambda q}(r_2) \]  

\[ (-F_{\sigma_2 \sigma_1}(r_2 \tau_2, r_1 \tau_1)) \]

\[
= \frac{1}{\beta^2} \int d^3 r_1 \int d^3 r_2 \sum_{\lambda q} \sum_{n_1 n_2} V_{\lambda q}(r_1) V_{\lambda q}(r_2) \times 
\]

\[ F(r_1, r_2; \omega_{n_1}) F'(r_2, r_1; \omega_{n_2}) \frac{2\Omega_{\lambda q}}{(i \omega_{n_1} - i \omega_{n_2})^2 - \Omega_{\lambda q}^2} \]

\[
= - \int d^3 r_1 \int d^3 r_2 \sum_{\lambda q} V_{\lambda q}(r_1) V_{\lambda q}(r_2) \sum_{ij} \left\{ 
\right. 
\]

\[ u_i(r_1) v_i^*(r_2) u_j^*(r_2) v_j(r_1) I(E_i, -E_j, \Omega_{\lambda q}) 
- u_i(r_1) v_i^*(r_2) v_j(r_2) u_j^*(r_1) I(E_i, E_j, \Omega_{\lambda q}) \]
\[ -v_i^*(r_1) u_i(r_2) u_j^*(r_2) v_j(r_1) I(-E_i, -E_j, \Omega_{\lambda q}) + v_i^*(r_1) u_i(r_2) v_j(r_2) u_j^*(r_1) I(-E_i, E_j, \Omega_{\lambda q}) \] 

(D.13)

In the decoupling approximation this yields:

\[
F \begin{array}{c}
\begin{array}{c}
    \hline
    \hline
    \hline
    \hline
\end{array}
\end{array}
\] =

\[
= - \sum_{\lambda q} \sum_{ij} |g_{ij}^{\lambda q}|^2 u_i v_i u_j v_j (2I(E_i, -E_j, \Omega_{\lambda q}) - 2I(E_i, E_j, \Omega_{\lambda q}))
\]

\[
= - \frac{1}{2} \sum_{\lambda q} \sum_{ij} |g_{ij}^{\lambda q}|^2 \sqrt{1 - \frac{(\epsilon_i - \mu)^2}{E_i}} \sqrt{1 - \frac{(\epsilon_j - \mu)^2}{E_j}} e^{i(\delta_i - \delta_j)} \times
\]

\[
\times (I(E_i, -E_j, \Omega_{\lambda q}) - I(E_i, E_j, \Omega_{\lambda q}))
\]

\[
= - \frac{1}{2} \sum_{\lambda q} \sum_{ij} |g_{ij}^{\lambda q}|^2 \frac{\Delta_i \Delta_j}{E_i E_j} (I(E_i, -E_j, \Omega_{\lambda q}) - I(E_i, E_j, \Omega_{\lambda q})) \]  

(D.14)

\[
F \begin{array}{c}
\begin{array}{c}
    \hline
    \hline
\end{array}
\end{array}
\] =

\[
= \frac{1}{\beta} \frac{(-1)^{l+1}}{1!} \int_0^\beta d\tau \int d^3r \sum_{\lambda q} \sum_{\sigma} (-G_{\sigma,\sigma}(r\tau, r\tau^+)) V^{(2)}_{\lambda q, \lambda q}(r) (-D_{\lambda q}(\tau^+ - \tau))
\]

\[
= \sum_{\lambda q} \int d^3r n(r) V^{(2)}_{\lambda q, \lambda q}(r) (2n_\beta(\Omega_{\lambda q}) + 1)
\]

\[
= \sum_{\lambda q} \int d^3r n(r) V^{(2)}_{\lambda q, \lambda q}(r) (2n_\beta(\Omega_{\lambda q}) + 1)
\]  

(D.15)

\[
F \begin{array}{c}
\begin{array}{c}
    \hline
    \hline
\end{array}
\end{array}
\] =

\[
= \frac{1}{\beta} \frac{(-1)^{l+1}}{1!} \int_0^\beta d\tau \int d^3r \sum_{\sigma} (-G_{\sigma,\sigma}(r\tau, r\tau^+)) (v_{\text{lat}}(r))
\]

\[
= \int d^3r n(r) v_{\text{lat}}(r)
\]  

(D.16)

\[
F \begin{array}{c}
\begin{array}{c}
    \hline
    \hline
    \hline
\end{array}
\end{array}
\] =

\[
= \int d^3r n(r) v_{\text{lat}}(r)
\]  

(D.16)
Appendix D. Evaluation of the first order diagrams

\[ F \left[ \begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{fig1.png}}
\end{array} \right] = \]

\[-\frac{1}{\beta} (-1)^{1+1} \frac{1}{1!} \int_0^\beta d\tau \int d^3r \sum_\sigma (-G_{\sigma,\sigma}(r r, r r^+))(-v_H(r)) \]

\[ = - \int d^3r n(r) v_H(r) \]

\[ = - \int d^3r \int d^3r' \frac{n(r)n(r')}{|r - r'|} \] (D.17)

\[ F \left[ \begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{fig2.png}}
\end{array} \right] = \]

\[-\frac{1}{\beta} (-1)^{1+1} \frac{1}{1!} \int_0^\beta d\tau \int d^3r \sum_\sigma (-G_{\sigma,\sigma}(r r, r r^+))(-v_H^{ie}(r)) \]

\[ = - \int d^3r n(r)v_H^{ie}(r) \] (D.18)

\[ F \left[ \begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{fig3.png}}
\end{array} \right] = \]

\[-\frac{1}{\beta} (-1)^{1+1} \frac{1}{1!} \int_0^\beta d\tau \int d^3r \sum_\sigma (-G_{\sigma,\sigma}(r r, r r^+))(-v_{xc}(r)) \]

\[ = - \int d^3r n(r)v_{xc}(r) \] (D.19)

\[ F \left[ \begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{fig4.png}}
\end{array} \right] = \]

\[-\frac{1}{\beta} (-1)^{1+1+1} \frac{1}{1!} \int_0^\beta d\tau \int d^3r_1 \int d^3r_2 \sum_{\sigma_1\sigma_2} (-F_{\sigma_1\sigma_2}^t(r_1\tau, r_2\tau^+))(-\frac{1}{2}\delta_{\sigma_1, -\sigma_2}\Delta_{xc}(r_1, r_2)) \]

\[ = \int d^3r_1 \int d^3r_2 \chi^*(r_1, r_2) \Delta_{xc}(r_1, r_2) \] (D.20)

\[ F \left[ \begin{array}{c}
\text{\includegraphics[width=0.2\textwidth]{fig5.png}}
\end{array} \right] = \]

\[-\frac{1}{\beta} (-1)^{1+1+1} \frac{1}{1!} \int_0^\beta d\tau \int d^3r_1 \int d^3r_2 \sum_{\sigma_1\sigma_2} (-F_{\sigma_1\sigma_2}(r_1\tau, r_2\tau^+))(-\frac{1}{2}\delta_{\sigma_1, -\sigma_2}\Delta_{xc}^*(r_1, r_2)) \]

\[ = \int d^3r_1 \int d^3r_2 \chi(r_1, r_2) \Delta_{xc}^*(r_1, r_2) \] (D.21)
\[
F \left[ \begin{array}{c}
\begin{array}{c}
H \hline \hline \hline W \hline \hline H
\end{array}
\end{array} \right] =
\]
\[
= -\frac{1}{\beta} \frac{(-1)^{2+0}}{2!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_{\lambda q} (-V_{H,\lambda q})(-D_{\lambda q}(\tau_1 - \tau_2))(-V_{H,\lambda q})
\]
\[
= \frac{1}{2} \sum_{\lambda q} V_{H,\lambda q}^2 \left( \sum_{\nu} \left( \frac{1}{\beta^2} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 e^{i\omega_\nu(\tau_1 - \tau_2)} \right) \frac{2\Omega_{\lambda q}}{(i\omega_\nu)^2 - \Omega_{\lambda q}^2} \right)
\]
\[
= -\sum_{\lambda q} \frac{V_{H,\lambda q}^2}{\Omega_{\lambda q}}
\]
\[
= -\int d^3r_1 \int d^3r_2 n(r_1) \sum_{\lambda} \frac{V_{\lambda 0}(r_1)V_{\lambda 0}(r_2)}{\Omega_{\lambda 0}} n(r_2)
\]  \quad (D.22)

\[
F \left[ \begin{array}{c}
\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
H \hline \hline \hline W \hline \hline H
\end{array}
\end{array}
\end{array}
\end{array} \right] =
\]
\[
= -\frac{2}{\beta} \frac{(-1)^{2+0}}{1! 1!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_{\lambda q} (-V_{H,\lambda q})(-D_{\lambda q}(\tau_1 - \tau_2))(-V_{xc,\lambda q})
\]
\[
= \sum_{\lambda q} \frac{2V_{xc,\lambda q}}{\Omega_{\lambda q}} \left( \int d^3r n(r) V_{\lambda q}(r) \right)
\]  \quad (D.23)

\[
F \left[ \begin{array}{c}
\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
xc \hline \hline \hline xc
\end{array}
\end{array}
\end{array}
\end{array} \right] =
\]
\[
= -\frac{1}{\beta} \frac{(-1)^{2+0}}{2!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \sum_{\lambda q} (-V_{xc,\lambda q})(-D_{\lambda q}(\tau_1 - \tau_2))(-V_{xc,\lambda q})
\]
\[
= \sum_{\lambda q} \frac{V_{xc,\lambda q}^2}{\Omega_{\lambda q}}
\]  \quad (D.24)

\[
F \left[ \begin{array}{c}
\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
xc \hline \hline \hline xc
\end{array}
\end{array}
\end{array}
\end{array} \right] =
\]
\[
= -\frac{2}{\beta} \frac{(-1)^{2+1}}{1! 1!} \int_0^\beta d\tau_1 \int_0^\beta d\tau_2 \int d^3r \sum_{\sigma} \sum_{\lambda q} (-G_{\sigma,\sigma}(r\tau_1, r\tau_2^+)) \times
\]
\[\times V_{\lambda q}(r)(-D_{\lambda q}(\tau_1 - \tau_2))(-V_{\lambda q})\]
\[= - \int d^3r \sum_{\lambda q} n(r)V_{\lambda q}(r) \frac{2V_{\lambda q}}{\Omega_{\lambda q}}\]
\[= \int d^3r_1 \int d^3r_2 n(r_1) \sum_{\lambda} \frac{2V_{\lambda 0}(r_1) V_{\lambda 0}(r_2)}{\Omega_{\lambda 0}} n(r_2) \quad (D.25)\]

\[F\left[ \begin{array}{c}
\text{\includegraphics[width=1cm]{DiagramA}}
\end{array} \right] = \]
\[= - \frac{2 (-1)^{2+1}}{\beta 1! 1!} \int_0^\beta d\tau_1 \int_0^{\beta} d\tau_2 \int d^3r \sum_{\lambda q} \sum_{\sigma} (-G_{\sigma,\sigma}(r\tau_1, r\tau_2^+)) \times V_{\lambda q}(r)(-D_{\lambda q}(\tau_1 - \tau_2))(-V_{\lambda q})\]
\[= - \sum_{\lambda q} \frac{2V_{\lambda q}}{\Omega_{\lambda q}} \left( \int d^3r n(r)V_{\lambda q}(r) \right) \quad (D.26)\]

\[F\left[ \begin{array}{c}
\text{\includegraphics[width=1cm]{DiagramB}}
\end{array} \right] = \]
\[= - \frac{1 (-1)^{1+0}}{\beta 1!} \int_0^{\beta} d\tau \sum_{\lambda q} (-V_{\lambda q}^{(2)})(-D_{\lambda q}(\tau^+ - \tau))\]
\[= \sum_{\lambda q} V_{\lambda q}^{(2)}(2n_{\beta}(\Omega_{\lambda q}) + 1)\]
\[= - \int d^3r \sum_{\lambda q} n(r)V_{\lambda q}^{(2)}(2n_{\beta}(\Omega_{\lambda q}) + 1)\]
\[= - \int d^3r \sum_{\lambda} n(r)V_{\lambda q}^{(2)}(2n_{\beta}(\Omega_{\lambda q}) + 1) \quad (D.27)\]

\[F\left[ \begin{array}{c}
\text{\includegraphics[width=1cm]{DiagramC}}
\end{array} \right] = \]
\[= - \frac{1 (-1)^{1+0}}{\beta 1!} \int_0^{\beta} d\tau \sum_{\lambda q} (-V_{\lambda q}^{(2)})(-D_{\lambda q}(\tau^+ - \tau))\]
\[= - \sum_{\lambda q} V_{\lambda q}^{(2)}(2n_{\beta}(\Omega_{\lambda q}) + 1) \quad (D.28)\]
Appendix E

Evaluation of the Matsubara sums

The expression to be calculated is

$$I(E_i, E_j, \Omega) = \frac{1}{\beta^2} \sum_{n_1 n_2} \frac{1}{i \omega_{n_1} - E_i} \frac{1}{i \omega_{n_2} - E_j} \frac{2\Omega}{(i \omega_{n_1} - i \omega_{n_2})^2 - \Omega^2}. \tag{E.1}$$

Before performing these sums, we consider the expression

$$g(E_1, E_2) := \frac{1}{\beta} \sum_n \frac{1}{i \omega_n - E_1} \frac{1}{i \omega_n - E_2}. \tag{E.2}$$

As shown in [36] this can be evaluated by inserting a redundant convergence factor $e^{i \omega_n \eta}$ and splitting the expression in partial fractions:

$$g(E_1, E_2) = \frac{1}{\beta} \sum_n \frac{1}{E_1 - E_2} \left( \lim_{\eta \to 0} \frac{1}{\beta} \sum_n e^{i \omega_n \eta} - \lim_{\eta \to 0} \frac{1}{\beta} \sum_n \frac{e^{i \omega_n \eta}}{i \omega_n - E_2} \right). \tag{E.3}$$

The sums can now be evaluated as

$$\lim_{\eta \to 0} \frac{1}{\beta} \sum_n \frac{e^{i \omega_n \eta}}{i \omega_n - E} = f_\beta(E) \tag{E.4}$$

where $f_\beta(E)$ is the Fermion distribution function. Thus one obtains:

$$g(E_1, E_2) = \frac{f_\beta(E_1) - f_\beta(E_2)}{E_1 - E_2}. \tag{E.5}$$

The term (E.1) can be rewritten as

$$I(E_i, E_j, \Omega) = J(E_i, E_j, \Omega) - J(E_i, E_j, -\Omega) \tag{E.6}$$

with

$$J(E_i, E_j, \Omega) = \frac{1}{\beta^2} \sum_{n_1 n_2} \frac{1}{i \omega_{n_1} - E_i} \frac{1}{i \omega_{n_2} - E_j} \frac{1}{i \omega_{n_1} - i \omega_{n_2} - \Omega}. \tag{E.7}$$

Using Eq. (E.5) for evaluating the $n_1$ summation yields:

$$J(E_i, E_j, \Omega) = \frac{1}{\beta} \sum_{n_2} \frac{1}{i \omega_{n_2} - E_j} \frac{f_\beta(i \omega_{n_2} + \Omega) - f_\beta(E_i)}{(i \omega_{n_2} + \Omega) - E_i}. \tag{E.8}$$
It is easy to see that

$$f_\beta(i\omega_n + \Omega) = -n_\beta(\Omega)$$  \hspace{1cm} (E.9)

where $\omega_n$ is a Fermionic Matsubara frequency and $n_\beta(\Omega)$ is the Bose distribution function. With this and a second application of Eq. (E.5) we get

$$J(E_i, E_j, \Omega) = \frac{1}{E_i - E_j - \Omega} (f_\beta(E_i) + n_\beta(\Omega)) (f_\beta(E_j) - f_\beta(E_i - \Omega)).$$  \hspace{1cm} (E.10)

Hence the complete term is found to be:

$$I(E_i, E_j, \Omega) = f_\beta(E_i) f_\beta(E_j) n_\beta(\Omega) \left( \frac{e^{\beta E_i} - e^{\beta(E_i+\Omega)}}{E_i - E_j - \Omega} - \frac{e^{\beta E_j} - e^{\beta(E_i+\Omega)}}{E_i - E_j + \Omega} \right).$$  \hspace{1cm} (E.11)
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Zusammenfassung

Bis heute gibt es keine befriedigende Methode, mit der man materialspezifische Eigenschaften supraleitender Systeme allein aufgrund theoretischer Berechnungen, d.h. ohne Anpassung freier Parameter an gemessene Größen, vorhersagen kann. Die BCS-Theorie liefert beispielsweise nur universelle Aussagen, wie etwa die skalierte Energielücke $\Delta/\Delta_0$ als Funktion der reduzierten Temperatur $T/T_c$, aber keine absoluten Größen. Für einfache Metalle, wie z.B. Aluminium, stimmen diese universellen Eigenschaften sehr gut mit experimentell messbaren Größen überein. Dies kann durch die sehr große Kohärenzlänge dieser Materialien verstanden werden, die sozusagen über die mikroskopische Struktur der Substanzen mittelt. Desweiteren sind in diesen einfachen Supraleitern Korrelationsbeiträge zur Supraleitung sehr klein, so daß eine Mean-Field-Theorie wie BCS schon gute Resultate liefert. Will man allerdings über die Beschreibung dieser einfachen Systeme hinausgehen, so wird es notwendig, sowohl die Inhomogenität des Systems, als auch Korrelationseffekte zu berücksichtigen.


Als erste Näherung wurden alle Diagramme niedrigster Ordnung betrachtet. Es zeigte sich, daß sich eine Reihe von Diagrammen, insbesondere die, die das auf die Kerne wirkende Hartree-Potential enthalten, gegenseitig kompensieren. Die verbleibenden Diagramme, die Hartree- oder Austausch-Korrelations-Potentiale enthalten, ergaben genau die Terme, die von dem störungstheoretisch berechneten Term zu subtrahieren waren, um das Austausch-Korrelations-Funktional zu erhalten. Die vier

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