

DENSITY FUNCTIONAL THEORY OF THE SUPERCONDUCTING STATE

E.K.U. Gross, Stefan Kurth, Klaus Capelle and Martin Lüders

Institut für Theoretische Physik
Universität Würzburg
Am Hubland
97074 Würzburg
Germany

1 Introduction

Traditional superconductivity of pure metals is well described as a phenomenon of **homogeneous** media. Due to the relatively large coherence length ($10^2 - 10^4$ Å), inhomogeneities on the scale of the lattice constant can be neglected. In the new high- T_c materials the situation is different. Experimental coherence lengths of the order of 10 Å suggest that inhomogeneities on the scale of the lattice constant have to be taken into account in a proper description of these materials.

The traditional description of superconductors by Bardeen, Cooper and Schrieffer (BCS) is based on a mean-field approximation [1]. For the BCS reduced Hamiltonian this mean-field approximation has been shown to be exact, i.e., correlation effects vanish in the thermodynamic limit [2]. This, however, is not necessarily true for more complicated interactions in inhomogeneous media.

The density functional formalism for superconductors presented in this paper provides a unified treatment of correlation effects in inhomogeneous superconductors. In the next section, Hohenberg-Kohn and Kohn-Sham-type theorems for superconductors are reviewed. The following section will be devoted to a brief discussion of the nature of the interaction. After that, in section 4, a diagrammatic formalism for superconductors is developed which, in section 5, is then exploited to construct an LDA-type functional for the exchange-correlation energy. In section 6, a current density functional theory for superconductors including spin degrees of freedom is developed and finally, in section 7, the frequency-dependent linear response of superconductors will be investigated.

We consider superconducting systems described by a grand-canonical Hamiltonian of the following form (atomic units are used throughout):

$$\begin{aligned} \hat{H} = & \sum_{\sigma=\uparrow\downarrow} \int d^3\mathbf{r} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\nabla^2}{2} + v(\mathbf{r}) - \mu \right) \hat{\Psi}_{\sigma}(\mathbf{r}) + \hat{U} + \hat{W} \\ & - \iint \left(D^*(\mathbf{r}, \mathbf{r}') \hat{\Psi}_{\uparrow}(\mathbf{r}) \hat{\Psi}_{\downarrow}(\mathbf{r}') + D(\mathbf{r}, \mathbf{r}') \hat{\Psi}_{\downarrow}^{\dagger}(\mathbf{r}') \hat{\Psi}_{\uparrow}^{\dagger}(\mathbf{r}) \right) d^3\mathbf{r} d^3\mathbf{r}'. \end{aligned} \quad (1)$$

where \hat{U} is the mutual Coulomb repulsion of the electrons

$$\hat{U} = \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma'}^{\dagger}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\Psi}_{\sigma'}(\mathbf{r}') \hat{\Psi}_{\sigma}(\mathbf{r}) \quad (2)$$

and \hat{W} is a (generally nonlocal) phonon-induced electron-electron interaction

$$\hat{W} = -\frac{1}{2} \sum_{\sigma, \sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \int d^3\mathbf{x} \int d^3\mathbf{x}' \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma'}^{\dagger}(\mathbf{r}') w(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \hat{\Psi}_{\sigma'}(\mathbf{x}) \hat{\Psi}_{\sigma}(\mathbf{x}'). \quad (3)$$

$v(\mathbf{r})$ is the Coulomb potential produced by a periodic lattice and $D(\mathbf{r}, \mathbf{r}')$ is an external pairing field which can be viewed as the proximity-induced field of an adjacent superconductor.

The density functional formalism, first proposed by Oliveira, Gross and Kohn (OGK) [3], provides a description of superconductors at finite temperatures in terms of two ‘‘densities’’: the normal density

$$n(\mathbf{r}) = \sum_{\sigma} \langle \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) \rangle \quad (4)$$

and the anomalous density

$$\Delta(\mathbf{r}, \mathbf{r}') = \langle \hat{\Psi}_{\uparrow}(\mathbf{r}) \hat{\Psi}_{\downarrow}(\mathbf{r}') \rangle. \quad (5)$$

The diagonal $\Delta(\mathbf{r}, \mathbf{r})$ can be shown [4] to be identical, in the appropriate limits, with the phenomenological order parameter of the Ginzburg-Landau theory [5].

In analogy to the temperature-dependent version [6] of the traditional Hohenberg-Kohn (HK) statement, OGK proved the existence of a 1-1 mapping of the **pair** of potentials $\{v(\mathbf{r}) - \mu, D(\mathbf{r}, \mathbf{r}')\}$ onto the **pair** of equilibrium densities $\{n(\mathbf{r}), \Delta(\mathbf{r}, \mathbf{r}')\}$. As a consequence the grand-canonical thermodynamic potential can be written as a functional of the densities:

$$\Omega[n, \Delta] = F[n, \Delta] + \int d^3\mathbf{r} n(\mathbf{r}) (v(\mathbf{r}) - \mu) - \int d^3\mathbf{r} \int d^3\mathbf{r}' (D^*(\mathbf{r}, \mathbf{r}') \Delta(\mathbf{r}, \mathbf{r}') + c.c.) \quad (6)$$

where $F[n, \Delta]$ is a universal functional depending only on the particle-particle interaction ($\hat{U} + \hat{W}$) but not on the external potentials $\{v(\mathbf{r}) - \mu, D(\mathbf{r}, \mathbf{r}')\}$ of the particular system considered. This means that a given superconducting material when exposed to various external fields only has one universal functional $F[n, \Delta]$. A different material, however, requires a different functional $F[n, \Delta]$ because the phonon-induced interaction \hat{W} will in general be different.

The theorem can be used to derive a set of self-consistent single-particle Kohn-Sham (KS)-type equations that determine, in principle exactly, the densities $n(\mathbf{r})$ and $\Delta(\mathbf{r}, \mathbf{r}')$ of the interacting system described by the Hamiltonian (1). At any given inverse temperature $\beta = 1/(k_B T)$ these equations are:

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu \right) u_k(\mathbf{r}) + \int D_s(\mathbf{r}, \mathbf{r}') v_k(\mathbf{r}') d^3\mathbf{r}' = E_k u_k(\mathbf{r}) \quad (7)$$

In terms of the functions $u_k(\mathbf{r})$ and $v_k(\mathbf{r})$ the densities are given by

$$n(\mathbf{r}) = 2 \sum_k (|u_k(\mathbf{r})|^2 f_\beta(E_k) + |v_k(\mathbf{r})|^2 f_\beta(-E_k)) \quad (9)$$

$$\Delta(\mathbf{r}, \mathbf{r}') = \sum_k (v_k^*(\mathbf{r}') u_k(\mathbf{r}) f_\beta(-E_k) - v_k^*(\mathbf{r}) u_k(\mathbf{r}') f_\beta(E_k)) \quad (10)$$

where f_β denotes the Fermi distribution

$$f_\beta(E) = \frac{1}{1 + e^{\beta E}}. \quad (11)$$

Eqs.(7) and (8) contain two effective single-particle potentials: the “normal” potential $v_s(\mathbf{r})$ and the effective pairing potential $D_s(\mathbf{r}, \mathbf{r}')$. Both are functionals of the normal and the anomalous density:

$$v_s[n, \Delta](\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' + v_{xc}^\beta[n, \Delta](\mathbf{r}) \quad (12)$$

$$\begin{aligned} D_s[n, \Delta](\mathbf{r}, \mathbf{r}') &= D(\mathbf{r}, \mathbf{r}') + \iint w(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Delta(\mathbf{x}, \mathbf{x}') d^3 \mathbf{x} d^3 \mathbf{x}' \\ &- \frac{\Delta(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + D_{xc}^\beta[n, \Delta](\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (13)$$

The exchange-correlation (xc) potentials are formally defined as functional derivatives of the xc-free-energy functional $F_{xc}^\beta[n, \Delta]$ which explicitly depends on temperature,

$$v_{xc}^\beta[n, \Delta](\mathbf{r}) = \frac{\delta F_{xc}^\beta[n, \Delta]}{\delta n(\mathbf{r})} \quad (14)$$

$$D_{xc}^\beta[n, \Delta](\mathbf{r}, \mathbf{r}') = -\frac{\delta F_{xc}^\beta[n, \Delta]}{\delta \Delta^*(\mathbf{r}, \mathbf{r}')}, \quad (15)$$

and $F_{xc}^\beta[n, \Delta]$ is defined by the equality

$$\begin{aligned} F[n, \Delta] &= T_s[n, \Delta] - \frac{1}{\beta} S_s[n, \Delta] \\ &+ \frac{1}{2} \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \frac{\Delta^*(\mathbf{r}, \mathbf{r}') \Delta(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \\ &- \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \int d^3 \mathbf{x} \int d^3 \mathbf{x}' \Delta^*(\mathbf{r}, \mathbf{r}') w(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Delta(\mathbf{x}, \mathbf{x}') + F_{xc}^\beta[n, \Delta]. \end{aligned} \quad (16)$$

Here $T_s[n, \Delta]$ and $S_s[n, \Delta]$ are the density functionals of the kinetic energy and the entropy of a non-interacting system.

Some arbitrariness is involved in the definition of the xc functional F_{xc}^β : it depends on the choice of the “Hartree” potentials treated as **seperate** terms in eqs. (12), (13) and (16). In the present definition, an anomalous Hartree term with respect to the Coulomb interaction is treated as separate term while OGK considered this term as part of the xc functional. The present choice allows one to treat the Coulomb and phonon-induced interactions **on the**

level estimation of the SC state. For practical calculations, however, the identification and separate treatment of appropriate Hartree terms is a very important matter because these terms, being the **dominant** diagrams of the **inhomogeneous** system, are treated in eqs. (12) and (13) **without any approximation**. By contrast, all other diagrammatic contributions to the total free energy of the inhomogeneous system, subsumed in the functional F_{xc}^β , are treated, in practice, only **approximately**, e.g. in terms of an LDA-type approximation.

Since v_s and D_s depend on the densities the whole set of equations (7) to (15) has to be solved self-consistently. Eqs. (7) and (8) are structurally similar to the Bogoliubov-deGennes equations [7], but - in contrast to the latter - include xc effects in principle exactly.

Numerical solutions of eqs. (7) - (15) can be constructed from the “normal” Bloch type KS orbitals satisfying

$$\left(-\frac{\nabla^2}{2} + v_s[n, \Delta](\mathbf{r}) \right) \varphi_{\alpha, \mathbf{k}}(\mathbf{r}) = \varepsilon_{\alpha, \mathbf{k}} \varphi_{\alpha, \mathbf{k}}(\mathbf{r}) \quad (17)$$

with the potential (12). The orbitals $\varphi_{\alpha, \mathbf{k}}$ are symmetry-adapted wave functions; the index α labels the point group symmetries of the lattice while \mathbf{k} denotes the crystal momentum. If the pair potential, $D_s(\mathbf{r}, \mathbf{r}')$, has the same translational and point symmetries as the normal KS potential, $v_s(\mathbf{r})$, the matrix elements

$$D_{\alpha, \mathbf{k}; \beta, \mathbf{q}} = \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \varphi_{\alpha, \mathbf{k}}^*(\mathbf{r}) D_s(\mathbf{r}, \mathbf{r}') \varphi_{\beta, \mathbf{q}}^*(\mathbf{r}') \quad (18)$$

(where $\tilde{\beta}, \tilde{\mathbf{q}}$ are the quantum numbers of the time-reversed orbital $T[\varphi_{\beta, \mathbf{q}}]$) take a particularly simple form: with $\tilde{\mathbf{k}}$ and $\tilde{\mathbf{q}}$ in the first Brillouin zone and reciprocal lattice vectors \mathbf{K} and \mathbf{Q} one finds [8]

$$D_{\alpha, (\tilde{\mathbf{k}}+\mathbf{K}); \beta, (\tilde{\mathbf{q}}+\mathbf{Q})} = \delta_{\alpha, \beta} \delta_{\tilde{\mathbf{k}}, \tilde{\mathbf{q}}} D_{\alpha, (\tilde{\mathbf{k}}+\mathbf{K}); \alpha, (\tilde{\mathbf{k}}+\mathbf{Q})} \quad (19)$$

Considerable simplification is achieved if the coupling between different bands is neglected by setting $D_{\alpha, (\tilde{\mathbf{k}}+\mathbf{K}); \alpha, (\tilde{\mathbf{k}}+\mathbf{Q})} = 0$ for $\mathbf{K} \neq \mathbf{Q}$.¹ Within this approximation, the Bogoliubov-type equations (7) and (8) are diagonalized by the functions

$$u_{\alpha, \mathbf{k}}(\mathbf{r}) = u_{\alpha, \mathbf{k}} \varphi_{\alpha, \mathbf{k}}(\mathbf{r}), \quad v_{\alpha, \mathbf{k}}(\mathbf{r}) = v_{\alpha, \mathbf{k}} \varphi_{\tilde{\alpha}, \tilde{\mathbf{k}}}^*(\mathbf{r}) \quad (20)$$

with energy eigenvalues

$$E_{\alpha, \mathbf{k}} = \pm R_{\alpha, \mathbf{k}}, \quad R_{\alpha, \mathbf{k}} = \sqrt{(\varepsilon_{\alpha, \mathbf{k}} - \mu)^2 + |D_s(\alpha, \mathbf{k})|^2} \quad (21)$$

and

$$D_s(\alpha, \mathbf{k}) = D_{\alpha, \mathbf{k}; \alpha, \mathbf{k}} = \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \varphi_{\alpha, \mathbf{k}}^*(\mathbf{r}) \varphi_{\tilde{\alpha}, \tilde{\mathbf{k}}}^*(\mathbf{r}') D_s(\mathbf{r}, \mathbf{r}'). \quad (22)$$

The complex numbers $u_{\alpha, \mathbf{k}}, v_{\alpha, \mathbf{k}}$ in eq. (20) are given by

$$v_{\alpha, \mathbf{k}} = \frac{1}{\sqrt{2}} \left[1 - \frac{\varepsilon_{\alpha, \mathbf{k}} - \mu}{E_{\alpha, \mathbf{k}}} \right]^{\frac{1}{2}} \quad (23)$$

¹The coupling between different bands can be taken into account, e.g., by treating the matrix elements $D_{\alpha, (\tilde{\mathbf{k}}+\mathbf{K}); \alpha, (\tilde{\mathbf{k}}+\mathbf{Q})}$ for $\mathbf{K} \neq \mathbf{Q}$ perturbatively. First-order perturbation theory gives no correction to the spectrum (21) indicating that the neglect of interband coupling is a good approximation [8].

where

$$e^{i\delta_{\alpha,\mathbf{k}}} = \frac{D_s(\alpha, \mathbf{k})}{|D_s(\alpha, \mathbf{k})|}. \quad (25)$$

The densities then read

$$n(\mathbf{r}) = \sum_{\alpha, \mathbf{k}} \left(1 - \frac{\varepsilon_{\alpha, \mathbf{k}} - \mu}{R_{\alpha, \mathbf{k}}} \tanh\left(\frac{\beta}{2} R_{\alpha, \mathbf{k}}\right) \right) |\varphi_{\alpha, \mathbf{k}}(\mathbf{r})|^2 \quad (26)$$

and

$$\Delta(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_{\alpha, \mathbf{k}} \frac{D_s(\alpha, \mathbf{k})}{R_{\alpha, \mathbf{k}}} \tanh\left(\frac{\beta}{2} R_{\alpha, \mathbf{k}}\right) \varphi_{\alpha, \mathbf{k}}(\mathbf{r}) \varphi_{\bar{\alpha}, \bar{\mathbf{k}}}(\mathbf{r}'). \quad (27)$$

Insertion of (13) into (22) leads to the following integral equation for $D_s(\alpha, \mathbf{k})$:

$$\begin{aligned} D_s(\alpha, \mathbf{k}) &= D(\alpha, \mathbf{k}) \\ &+ \frac{1}{2} \sum_{\alpha', \mathbf{k}'} \frac{(w_P(\alpha \mathbf{k}, \alpha' \mathbf{k}') - w_C(\alpha \mathbf{k}, \alpha' \mathbf{k}')) D_s(\alpha', \mathbf{k}')}{R_{\alpha', \mathbf{k}'}} \tanh\left(\frac{\beta R_{\alpha', \mathbf{k}'}}{2}\right) \\ &+ D_{xc}[D_s](\alpha, \mathbf{k}) \end{aligned} \quad (28)$$

where w_P and w_C are given by

$$\begin{aligned} w_P(\alpha \mathbf{k}, \alpha' \mathbf{k}') &= \\ &= \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \int d^3 \mathbf{x} \int d^3 \mathbf{x}' \varphi_{\alpha, \mathbf{k}}^*(\mathbf{r}) \varphi_{\bar{\alpha}, \bar{\mathbf{k}}}^*(\mathbf{r}') w(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \varphi_{\alpha', \mathbf{k}'}(\mathbf{x}) \varphi_{\bar{\alpha}', \bar{\mathbf{k}'}}(\mathbf{x}'), \end{aligned} \quad (29)$$

$$w_C(\alpha \mathbf{k}, \alpha' \mathbf{k}') = \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 \varphi_{\alpha, \mathbf{k}}^*(\mathbf{r}_1) \varphi_{\bar{\alpha}, \bar{\mathbf{k}}}^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_{\alpha', \mathbf{k}'}(\mathbf{r}_2) \varphi_{\bar{\alpha}', \bar{\mathbf{k}'}}(\mathbf{r}_1) \quad (30)$$

and $D(\alpha, \mathbf{k})$ and $D_{xc}(\alpha, \mathbf{k})$ are defined in analogy to eq. (22).

In practice, one starts with an ordinary KS calculation for the material in question, i.e. one solves (17) with v_s given by

$$v_s[n](\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 \mathbf{r}' + v_{xc}[n](\mathbf{r}). \quad (31)$$

From this calculation we obtain single-particle orbitals $\varphi_{\alpha, \mathbf{k}}(\mathbf{r})$ and single-particle energies $\varepsilon_{\alpha, \mathbf{k}}$. With these $\varepsilon_{\alpha, \mathbf{k}}$, and with $w_P(\alpha \mathbf{k}, \alpha' \mathbf{k}')$ and $w_C(\alpha \mathbf{k}, \alpha' \mathbf{k}')$ resulting from the $\varphi_{\alpha, \mathbf{k}}(\mathbf{r})$ via (29) and (30), we solve the integral equation (28) for D_s and calculate the densities via eqs. (26) and (27). Insertion into (12) then yields a new single-particle potential v_s and we start again with eq. (17). The whole cycle is repeated until self-consistency is achieved.

The separation of the original equations (7) - (15) into a traditional KS equation (17) and a BCS type gap equation (28) is of particular importance because it achieves a separation of energy scales: the gap function $D_s(\alpha \mathbf{k})$ is typically three orders of magnitude smaller than characteristic features, such as band gaps, of the normal band structure $\varepsilon_{\alpha, \mathbf{k}}$. Furthermore, the dependence of the single-particle potential (12) on Δ is expected to be small, so that a self-consistent solution of the traditional KS scheme (i.e. with the single-particle potential $v_s[n]$ of (31)) will be very close to the result of the full self-consistency cycle (18), (26) - (30).

$$\varphi_k(\mathbf{r}) \sim e^{i\mathbf{k}\mathbf{r}}, \quad \varepsilon_k = \frac{k^2}{2}, \quad (32)$$

and eq. (28) reduces rigorously to the BCS gap equation if D_{xc} is neglected. Thus the traditional BCS model can be viewed as the homogeneous Hartree limit of the density functional theory for superconductors presented here. In order to go beyond BCS one needs approximations for the functional $D_{xc}[D_s]$. The construction of an LDA-type approximation for D_{xc} will be the objective of sections 4 and 5.

3 The Nature of the Interaction

At this point it is appropriate to make some remarks about the nature of the interaction $w(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}')$. We will discuss the physical ideas and approximations underlying the description of a superconducting many-electron system by the Hamiltonian (1). This will also lead us to an explicit approximation for the form of the interaction w .

The starting point of our discussion is the Hamiltonian of a many-electron system interacting with the vibrations of the crystal lattice:

$$\hat{H} = \hat{H}_{el} + \hat{H}_{ph} + \hat{H}_{el-ph} \quad (33)$$

where

$$\begin{aligned} \hat{H}_{el} = & \sum_{\sigma=\uparrow\downarrow} \int d^3\mathbf{r} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\nabla^2}{2} + v(\mathbf{r}) - \mu \right) \hat{\Psi}_{\sigma}(\mathbf{r}) \\ & + \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma'}^{\dagger}(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\Psi}_{\sigma'}(\mathbf{r}') \hat{\Psi}_{\sigma}(\mathbf{r}) \end{aligned} \quad (34)$$

is the Hamiltonian of interacting electrons moving in the electrostatic potential $v(\mathbf{r})$ of the fixed crystal lattice with all the ions in their equilibrium positions.

$$\hat{H}_{ph} = \sum_{\mathbf{q} \in BZ} \omega_{\mathbf{q}} \left(\hat{b}_{\mathbf{q}}^{\dagger} \hat{b}_{\mathbf{q}} + \frac{1}{2} \right) \quad (35)$$

is the Hamiltonian of the phonon system with bosonic operators $\hat{b}_{\mathbf{q}}^{\dagger}$ and $\hat{b}_{\mathbf{q}}$. The sum runs over all wave vectors in the first Brillouin zone. For simplicity we restrict ourselves to only one phonon branch. \hat{H}_{el-ph} is the Hamiltonian of the electron-phonon interaction of which the explicit form will be given later. The formal steps to arrive at (33) starting from the full electron-ion system can be found, e.g., in [9].

As a first approximation we treat the purely electronic problem, the Hamiltonian \hat{H}_{el} , within the usual Kohn-Sham scheme, i.e. we replace \hat{H}_{el} by

$$\hat{H}_{el}^{KS} = \sum_{\alpha\mathbf{k}\sigma} (\varepsilon_{\alpha,\mathbf{k}} - \mu) \hat{c}_{\alpha,\mathbf{k},\sigma}^{\dagger} \hat{c}_{\alpha,\mathbf{k},\sigma} \quad (36)$$

where α is a band index and \mathbf{k} the crystal momentum. The $\varepsilon_{\alpha,\mathbf{k}}$ are the eigenvalues of the Kohn-Sham equation

$$\left(-\frac{\nabla^2}{2} + v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}[n](\mathbf{r}) \right) \varphi_{\alpha,\mathbf{k}}(\mathbf{r}) = \varepsilon_{\alpha,\mathbf{k}} \varphi_{\alpha,\mathbf{k}}(\mathbf{r}) \quad (37)$$

states $\psi_{\alpha,\mathbf{k}}$ with spin σ , respectively. Similarly we shall formulate the electron-electron Coulomb interaction. Replacing \hat{H}_{el} by \hat{H}_{el}^{KS} is only for the momentary purpose of deriving a phonon-induced electron-electron interaction.

For the electron-phonon interaction \hat{H}_{el-ph} we can now write the explicit expression

$$\hat{H}_{el-ph} = \sum_{\alpha,\sigma} \sum_{\substack{\mathbf{k},\mathbf{q} \\ \in BZ}} V_{\mathbf{q}} (\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^{\dagger}) \hat{c}_{\alpha,\mathbf{k}+\mathbf{q},\sigma}^{\dagger} \hat{c}_{\alpha,\mathbf{k},\sigma}. \quad (38)$$

This form of the electron-phonon interaction is already the result of some simplification obtained by neglecting the so-called Umklapp processes. The matrix element $V_{\mathbf{q}}$ is basically the Fourier component of the gradient of the electron-ion interaction potential.

As the next step of our consideration we transform the Hamiltonian

$$\hat{H}' = \hat{H}_{el}^{KS} + \hat{H}_{ph} + \hat{H}_{el-ph} \quad (39)$$

by means of a canonical transformation first introduced by Fröhlich [10] and Bardeen and Pines [11]:

$$\hat{H}'' = e^{-\hat{S}} \hat{H}' e^{\hat{S}}. \quad (40)$$

Expanding the exponential we obtain up to second order in \hat{S} :

$$\hat{H}'' = \hat{H}' + [\hat{H}', \hat{S}] + \frac{1}{2} [[\hat{H}', \hat{S}], \hat{S}] + O(\hat{S}^3). \quad (41)$$

Now we choose the transformation operator \hat{S} such that

$$\hat{H}_{el-ph} + [\hat{H}_{el}^{KS} + \hat{H}_{ph}, \hat{S}] = 0. \quad (42)$$

This leads to

$$\hat{S} = \sum_{\alpha,\sigma} \sum_{\substack{\mathbf{k},\mathbf{q} \\ \in BZ}} \left(\frac{V_{\mathbf{q}}}{\varepsilon_{\alpha,\mathbf{k}} - \varepsilon_{\alpha,\mathbf{k}+\mathbf{q}} + \omega_{\mathbf{q}}} \hat{b}_{\mathbf{q}} + \frac{V_{\mathbf{q}}}{\varepsilon_{\alpha,\mathbf{k}} - \varepsilon_{\alpha,\mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}}} \hat{b}_{-\mathbf{q}}^{\dagger} \right) \hat{c}_{\alpha,\mathbf{k}+\mathbf{q},\sigma}^{\dagger} \hat{c}_{\alpha,\mathbf{k},\sigma}. \quad (43)$$

and up to second order in \hat{S} the transformed Hamiltonian reads

$$\hat{H}'' = \hat{H}_{el}^{KS} + \hat{H}_{ph} + \hat{H}_{BP} + \hat{H}_r \quad (44)$$

where

$$\hat{H}_{BP} = \sum_{\alpha,\alpha'} \sum_{\substack{\mathbf{k},\mathbf{k}',\mathbf{q} \\ \in BZ}} \sum_{\sigma,\sigma'} \frac{\omega_{\mathbf{q}} |V_{\mathbf{q}}|^2}{(\varepsilon_{\alpha',\mathbf{k}'} - \varepsilon_{\alpha',\mathbf{k}'-\mathbf{q}})^2 - \omega_{\mathbf{q}}^2} \hat{c}_{\alpha,\mathbf{k}+\mathbf{q},\sigma}^{\dagger} \hat{c}_{\alpha',\mathbf{k}'-\mathbf{q},\sigma'}^{\dagger} \hat{c}_{\alpha',\mathbf{k}',\sigma'} \hat{c}_{\alpha,\mathbf{k},\sigma} \quad (45)$$

and

$$\begin{aligned} \hat{H}_r = & \sum_{\alpha,\sigma} \sum_{\substack{\mathbf{k},\mathbf{q} \\ \in BZ}} \frac{\omega_{\mathbf{q}} |V_{\mathbf{q}}|^2}{(\varepsilon_{\alpha,\mathbf{k}} - \varepsilon_{\alpha,\mathbf{k}-\mathbf{q}})^2 - \omega_{\mathbf{q}}^2} \hat{c}_{\alpha,\mathbf{k},\sigma}^{\dagger} \hat{c}_{\alpha,\mathbf{k},\sigma} \\ & + \sum_{\alpha,\sigma} \sum_{\substack{\mathbf{k},\mathbf{q},\mathbf{q}' \\ \in BZ}} \left(A(\alpha, \mathbf{k}, \mathbf{k}', \mathbf{q}) \hat{b}_{\mathbf{q}'} + B(\alpha, \mathbf{k}, \mathbf{k}', \mathbf{q}) \hat{b}_{-\mathbf{q}'}^{\dagger} \right) (\hat{b}_{\mathbf{q}} + \hat{b}_{-\mathbf{q}}^{\dagger}) \hat{c}_{\alpha,\mathbf{k}+\mathbf{q}+\mathbf{q}',\sigma}^{\dagger} \hat{c}_{\alpha,\mathbf{k},\sigma} \end{aligned} \quad (46)$$

with

$$A(\alpha, \mathbf{k}, \mathbf{k}', \mathbf{q}) = \frac{1}{2} V_{\mathbf{q}} V_{\mathbf{q}'} \left(\frac{1}{\varepsilon_{\alpha,\mathbf{k}} - \varepsilon_{\alpha,\mathbf{k}+\mathbf{q}} + \omega_{\mathbf{q}}} - \frac{1}{\varepsilon_{\alpha,\mathbf{k}+\mathbf{q}} - \varepsilon_{\alpha,\mathbf{k}+\mathbf{q}+\mathbf{q}'} + \omega_{\mathbf{q}}} \right) \quad (47)$$

$$B(\alpha, \mathbf{k}, \mathbf{k}', \mathbf{q}) = \frac{1}{2} V_{\mathbf{q}} V_{\mathbf{q}'} \left(\frac{1}{\epsilon_{\alpha, \mathbf{k}} - \epsilon_{\alpha, \mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}}} - \frac{1}{\epsilon_{\alpha, \mathbf{k}+\mathbf{q}} - \epsilon_{\alpha, \mathbf{k}+\mathbf{q}+\mathbf{q}'} - \omega_{\mathbf{q}}} \right). \quad (48)$$

For the moment we neglect \hat{H}_r and resubstitute the electronic Kohn-Sham Hamiltonian \hat{H}_{el}^{KS} by the original electronic Hamiltonian \hat{H}_{el} . Adding an additional external pairing field we arrive (for the electronic part) at the Hamiltonian (1) with the Bardeen-Pines interaction

$$w_{BP}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') = - \sum_{\alpha, \alpha'} \sum_{\substack{\mathbf{k}, \mathbf{k}', \mathbf{q} \\ \in BZ}} \frac{2\omega_{\mathbf{q}} |V_{\mathbf{q}}|^2}{(\epsilon_{\alpha', \mathbf{k}'} - \epsilon_{\alpha', \mathbf{k}'-\mathbf{q}})^2 - \omega_{\mathbf{q}}^2} \varphi_{\alpha', \mathbf{k}'-\mathbf{q}}(\mathbf{r}) \varphi_{\alpha, \mathbf{k}+\mathbf{q}}(\mathbf{r}') \varphi_{\alpha, \mathbf{k}}^*(\mathbf{x}) \varphi_{\alpha', \mathbf{k}'}^*(\mathbf{x}'). \quad (49)$$

It is possible to incorporate the effects of \hat{H}_r in a plausible way by the following argument: treating \hat{H}_r within first order perturbation theory with respect to the single-particle state $|\alpha \mathbf{k} \sigma\rangle = \hat{c}_{\alpha, \mathbf{k}, \sigma}^\dagger |vac\rangle$ one obtains an energy correction $\delta \epsilon_{\alpha, \mathbf{k}}$ to the single-particle energy $\epsilon_{\alpha, \mathbf{k}}$:

$$\delta \epsilon_{\alpha, \mathbf{k}} = \langle \alpha \mathbf{k} \sigma | \hat{H}_r | \alpha \mathbf{k} \sigma \rangle = \sum_{\substack{\mathbf{q} \\ \in BZ}} \frac{|V_{\mathbf{q}}|^2}{\epsilon_{\alpha, \mathbf{k}} - \epsilon_{\alpha, \mathbf{k}+\mathbf{q}} - \omega_{\mathbf{q}}}. \quad (50)$$

This correction can be interpreted as a renormalization of the single-particle energy $\epsilon_{\alpha, \mathbf{k}}$, i.e. the effect of \hat{H}_r can eventually be taken into account by the replacement $\epsilon_{\alpha, \mathbf{k}} \longrightarrow \epsilon_{\alpha, \mathbf{k}} + \delta \epsilon_{\alpha, \mathbf{k}}$.

As we have described in the previous section, the form (1) of the Hamiltonian can be used as a starting point for the construction of a density functional theory for superconductors. If we decide not to solve the **full** self-consistency cycle (17), (26) - (30) but perform only the ordinary Kohn-Sham calculation (37) and use the resulting orbitals and orbital energies as **fixed** input for the gap equation, we achieve some further simplification. By virtue of the orthonormality of the Kohn-Sham orbitals $\varphi_{\alpha, \mathbf{k}}$, the formalism then leads to the gap equation

$$D_s(\alpha \mathbf{k}) = \frac{1}{2} \sum_{\alpha'} \sum_{\mathbf{k}'} \frac{(w_{BP}(\alpha \mathbf{k}, \alpha' \mathbf{k}') - w_C(\alpha \mathbf{k}, \alpha' \mathbf{k}')) D_s(\alpha' \mathbf{k}')}{R_{\alpha' \mathbf{k}'}} \tanh\left(\frac{\beta R_{\alpha' \mathbf{k}'}}{2}\right) + D_{xc}[D_s](\alpha \mathbf{k}) \quad (51)$$

with

$$w_{BP}(\alpha \mathbf{k}, \alpha' \mathbf{k}') = -\delta_{\alpha, \alpha'} \frac{2\omega_{\mathbf{k}+\mathbf{k}'} |V_{\mathbf{k}+\mathbf{k}'}|^2}{(\epsilon_{\alpha, \mathbf{k}} - \epsilon_{\alpha, \mathbf{k}'})^2 - \omega_{\mathbf{k}+\mathbf{k}'}^2} \quad (52)$$

and

$$w_C(\alpha \mathbf{k}, \alpha' \mathbf{k}') = \int d^3 \mathbf{r}_1 \int d^3 \mathbf{r}_2 \varphi_{\alpha, \mathbf{k}}^*(\mathbf{r}_1) \varphi_{\alpha', \mathbf{k}'}^*(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_{\alpha', \mathbf{k}'}(\mathbf{r}_2) \varphi_{\alpha, \mathbf{k}}(\mathbf{r}_1). \quad (53)$$

4 Perturbation Theory for Superconductors

In this section we will develop the diagrammatic formalism of a many-body perturbation theory for superconducting systems. To this end we split the original Hamiltonian (1) into two parts

$$\hat{H} = \hat{H}^{(0)} + \tilde{W} \quad (54)$$

$$\begin{aligned}\hat{H}^{(0)} &= \sum_{\sigma=\uparrow\downarrow} \int d^3\mathbf{r} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\nabla^2}{2} + v(\mathbf{r}) - \mu \right) \hat{\psi}_{\sigma}(\mathbf{r}) \\ &- \int d^3\mathbf{r} \int d^3\mathbf{r}' \left(D^*(\mathbf{r}, \mathbf{r}') \hat{\psi}_{\uparrow}(\mathbf{r}) \hat{\psi}_{\downarrow}(\mathbf{r}') + D(\mathbf{r}, \mathbf{r}') \hat{\psi}_{\downarrow}^{\dagger}(\mathbf{r}') \hat{\psi}_{\uparrow}^{\dagger}(\mathbf{r}) \right)\end{aligned}\quad (55)$$

and

$$\begin{aligned}\tilde{W} &= \hat{U} + \hat{W} \\ &:= \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3\mathbf{r} \int d^3\mathbf{r}' \int d^3\mathbf{x} \int d^3\mathbf{x}' \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma'}^{\dagger}(\mathbf{r}') \tilde{w}_{\sigma, \sigma'}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \hat{\psi}_{\sigma'}(\mathbf{x}) \hat{\psi}_{\sigma}(\mathbf{x}').\end{aligned}\quad (56)$$

One has to emphasize that $\hat{H}^{(0)}$ already describes a superconducting system due to the external pairing potential $D(\mathbf{r}, \mathbf{r}')$. $\hat{H}^{(0)}$ can be diagonalized by the Bogoliubov-Valatin transformation [12]

$$\hat{\psi}_{\uparrow}(\mathbf{r}) = \sum_k (u_k(\mathbf{r}) \hat{\gamma}_{k\uparrow} - v_k^*(\mathbf{r}) \hat{\gamma}_{k\downarrow}^{\dagger}) \quad (57)$$

$$\hat{\psi}_{\downarrow}(\mathbf{r}) = \sum_k (u_k(\mathbf{r}) \hat{\gamma}_{k\downarrow} + v_k^*(\mathbf{r}) \hat{\gamma}_{k\uparrow}^{\dagger}) \quad (58)$$

with fermionic quasi-particle operators $\hat{\gamma}_{k\uparrow}, \hat{\gamma}_{k\downarrow}$. The $u_k(\mathbf{r}), v_k(\mathbf{r})$ satisfy eigenvalue equations with the same algebraic structure as (7) and (8) and can be determined, under the same assumption as before, in exactly the same manner.

The diagonalized Hamiltonian reads

$$\hat{H}^{(0)} = \sum_k (\varepsilon_k - \mu - R_k) + \sum_{k, \sigma} R_k \hat{\gamma}_{k, \sigma}^{\dagger} \hat{\gamma}_{k, \sigma} \quad (59)$$

with ε_k being the eigenvalues of the Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + v(\mathbf{r}) \right) \varphi_k(\mathbf{r}) = \varepsilon_k \varphi_k(\mathbf{r}) \quad (60)$$

and

$$R_k = \sqrt{(\varepsilon_k - \mu)^2 + |D(k)|^2} \quad (61)$$

where

$$D(k) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi_k^*(\mathbf{r}) \varphi_k^*(\mathbf{r}') D(\mathbf{r}, \mathbf{r}'). \quad (62)$$

The densities resulting from \hat{H}_0 are given by

$$n(\mathbf{r}) = \sum_k \left(1 - \frac{\varepsilon_k - \mu}{R_k} \tanh\left(\frac{\beta}{2} R_k\right) \right) |\varphi_k(\mathbf{r})|^2 \quad (63)$$

and

$$\Delta(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_k \frac{D(k)}{R_k} \tanh\left(\frac{\beta}{2} R_k\right) \varphi_k(\mathbf{r}) \varphi_k^*(\mathbf{r}'). \quad (64)$$

Every eigenstate of \hat{H}_0 is a simultaneous eigenstate of the “quasi-particle number operator”

$$\hat{N}_{\gamma} = \sum_{k, \sigma} \hat{\gamma}_{k, \sigma}^{\dagger} \hat{\gamma}_{k, \sigma}. \quad (65)$$

we are able to contract a perturbation theory in the same fashion as it is usually done for normal-state systems.

With the usual definition of the finite-temperature Heisenberg and interaction pictures of some operator \hat{O}

$$\text{Heisenberg picture : } \quad \hat{O}(\tau)_H = e^{\hat{H}\tau} \hat{O} e^{-\hat{H}\tau} \quad (66)$$

$$\text{interaction picture : } \quad \hat{O}(\tau)_I = e^{\hat{H}^{(0)}\tau} \hat{O} e^{-\hat{H}^{(0)}\tau}, \quad (67)$$

(where τ is an “imaginary time” to be identified with the inverse temperature) the “time” evolution operator in the interaction picture is given by

$$\hat{\mathcal{U}}(\tau, \tau') = e^{\hat{H}^{(0)}\tau} e^{-\hat{H}(\tau-\tau')} e^{-\hat{H}^{(0)}\tau}. \quad (68)$$

$\hat{\mathcal{U}}(\tau, \tau')$ satisfies the equation of motion

$$\frac{\partial}{\partial \tau} \hat{\mathcal{U}}(\tau, \tau') = -\tilde{W}(\tau)_I \hat{\mathcal{U}}(\tau, \tau') \quad (69)$$

which can formally be solved

$$\hat{\mathcal{U}}(\tau, \tau') = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_{\tau'}^{\tau} d\tau_1 \dots \int_{\tau'}^{\tau} d\tau_n \hat{T} (\tilde{W}(\tau_1)_I \dots \tilde{W}(\tau_n)_I). \quad (70)$$

\hat{T} is the time ordering operator defined for fermionic operators \hat{A}, \hat{B} by

$$\hat{T} (\hat{A}(\tau)\hat{B}(\tau')) = \begin{cases} \hat{A}(\tau)\hat{B}(\tau') & \text{if } \tau > \tau' \\ -\hat{B}(\tau')\hat{A}(\tau) & \text{if } \tau' > \tau \end{cases} \quad (71)$$

Now the grand-canonical partition function Z for the full interacting system can be expressed as

$$\frac{Z}{Z^{(0)}} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^{\beta} d\tau_1 \dots \int_0^{\beta} d\tau_n \text{tr} \left\{ \hat{\rho}^{(0)} \hat{T} (\tilde{W}(\tau_1)_I \dots \tilde{W}(\tau_n)_I) \right\} \quad (72)$$

where

$$Z^{(0)} = \text{tr} \left\{ e^{-\beta \hat{H}^{(0)}} \right\} \quad (73)$$

is the partition function and

$$\hat{\rho}^{(0)} = \frac{e^{-\beta \hat{H}^{(0)}}}{\text{tr} \left\{ e^{-\beta \hat{H}^{(0)}} \right\}} \quad (74)$$

the statistical density operator of the non-interacting system.

Expressing \tilde{W} in terms of the quasi-particle operators $\hat{\gamma}$ and using the complete set of eigenstates of $\hat{H}^{(0)}$ (and \hat{N}_{γ}) for the evaluation of the trace we are able to prove Wick's theorem. With the definition of the contraction of two operators $\hat{\alpha}_i, \hat{\alpha}_j$

$$\overline{\alpha_i(\tau_i)_I \alpha_j(\tau_j)_I} := \text{tr} \left\{ \hat{\rho}^{(0)} \hat{T} (\hat{\alpha}_i(\tau_i)_I \hat{\alpha}_j(\tau_j)_I) \right\} \quad (75)$$

Wick's theorem reads

$$\begin{aligned} & \text{tr} \left\{ \hat{\rho}^{(0)} \hat{T} \left(\dots \hat{\Psi}_{\sigma_i}(\mathbf{r}_i \tau_i)_I \dots \hat{\Psi}_{\sigma_j}^{\dagger}(\mathbf{r}_j \tau_j)_I \dots \right) \right\} = \\ & = \sum (\text{all completely contracted terms}) \end{aligned} \quad (76)$$

as in normal-state perturbation theory. Defining one normal and two anomalous one-particle Green's functions of the non-interacting system

$$G_{\sigma\sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau') := -\overbrace{\Psi_{\sigma}(\mathbf{r}\tau)_I \Psi_{\sigma'}^{\dagger}(\mathbf{r}'\tau')_I} \quad (77)$$

$$F_{\sigma\sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau') := -\overbrace{\Psi_{\sigma}(\mathbf{r}\tau)_I \Psi_{\sigma'}(\mathbf{r}'\tau')_I} \quad (78)$$

$$F_{\sigma\sigma'}^{(0)\dagger}(\mathbf{r}\tau, \mathbf{r}'\tau') := -\overbrace{\Psi_{\sigma}^{\dagger}(\mathbf{r}\tau)_I \Psi_{\sigma'}^{\dagger}(\mathbf{r}'\tau')_I} \quad (79)$$

we are now able to write down the Feynman rules for the diagrammatic evaluation of the expansion (72):

1. The non-interacting Green's functions are represented by

a) $G_{\sigma\sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau')$

b) $F_{\sigma\sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau')$

c) $F_{\sigma\sigma'}^{(0)\dagger}(\mathbf{r}\tau, \mathbf{r}'\tau')$

2. The interaction is represented by

$$\tilde{w}_{\sigma\sigma'}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$$

3. Green's functions beginning and ending at the same interaction line are interpreted as the following limits:

$$G_{\sigma, \sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau) := \lim_{\tau' \rightarrow \tau^+} G_{\sigma, \sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau')$$

$$F_{\sigma, \sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau) := \lim_{\tau' \rightarrow \tau^+} F_{\sigma, \sigma'}^{(0)}(\mathbf{r}\tau', \mathbf{r}'\tau)$$

$$F_{\sigma, \sigma'}^{(0)\dagger}(\mathbf{r}\tau, \mathbf{r}'\tau) := \lim_{\tau' \rightarrow \tau^+} F_{\sigma, \sigma'}^{(0)\dagger}(\mathbf{r}\tau', \mathbf{r}'\tau)$$

5. The sign of a graph of order n is $(-1)^{n+q}$ where q is the number of permutations needed to bring the field operators in proper order.

6. The numerical factor of a graph of order n is

$$\left\{ \begin{array}{c} \frac{1}{n!2} \\ \frac{1}{n!} \end{array} \right\} \text{ if the graph is } \left\{ \begin{array}{c} \text{symmetric} \\ \text{asymmetric} \end{array} \right\}$$

with respect to the central vertical axis.

In formulating rule no. 6 we used the linked cluster theorem which can be proved using the same arguments as in normal-state perturbation theory

$$\frac{Z}{Z^{(0)}} = \exp \left(\sum \text{all connected graphs} \right). \quad (80)$$

In Fig.1 we show all topologically distinct graphs contributing to the free energy of the system up to second order in the interaction.

5 Exchange-Correlation Contributions to the Gap Equation

In this section we shall present explicit results for the xc part F_{xc} of the free-energy functional obtained with the diagrammatic methods developed in the last section. The functional derivative (15) of F_{xc} with respect to the anomalous density then leads to the xc terms in the gap equation (28).

The explicit calculations will be done for the case of a homogeneous electron gas, i.e. for vanishing external potential $v(\mathbf{r}) \equiv 0$, and translationally as well as rotationally invariant pairing potentials $D(\mathbf{r}, \mathbf{r}') = D(|\mathbf{r} - \mathbf{r}'|)$. In this case the approximation made in eq. (20) becomes exact. The results obtained for the homogeneous case will then be used to construct a local density approximation (LDA) for the general, inhomogeneous case.

We treat the Coulomb and the Bardeen-Pines interaction simultaneously. The full interaction then takes the form

$$\tilde{w}_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} \delta(\mathbf{r} - \mathbf{x}') \delta(\mathbf{r}' - \mathbf{x}) - w_{BP}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \quad (81)$$

where $w_{BP}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}')$ is given by (49). In the homogeneous case the “normal” Kohn-Sham orbitals entering the Bardeen-Pines interaction are simply given by

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\mathcal{V}}} e^{i\mathbf{k}\mathbf{r}} \quad (82)$$

with \mathcal{V} being the volume of the system. We perform the calculations to first order in the interaction (81). Beginning in second order, some of the diagrams contributing to the partition function are divergent (like for the normal-state homogeneous electron gas). This is due to the long-range nature of the bare Coulomb interaction. A resummation of these divergent graphs to infinite order will be necessary to obtain finite, physically meaningful results. In normal-state perturbation theory the simplest resummation of this kind is known as the random phase approximation (RPA) [13].

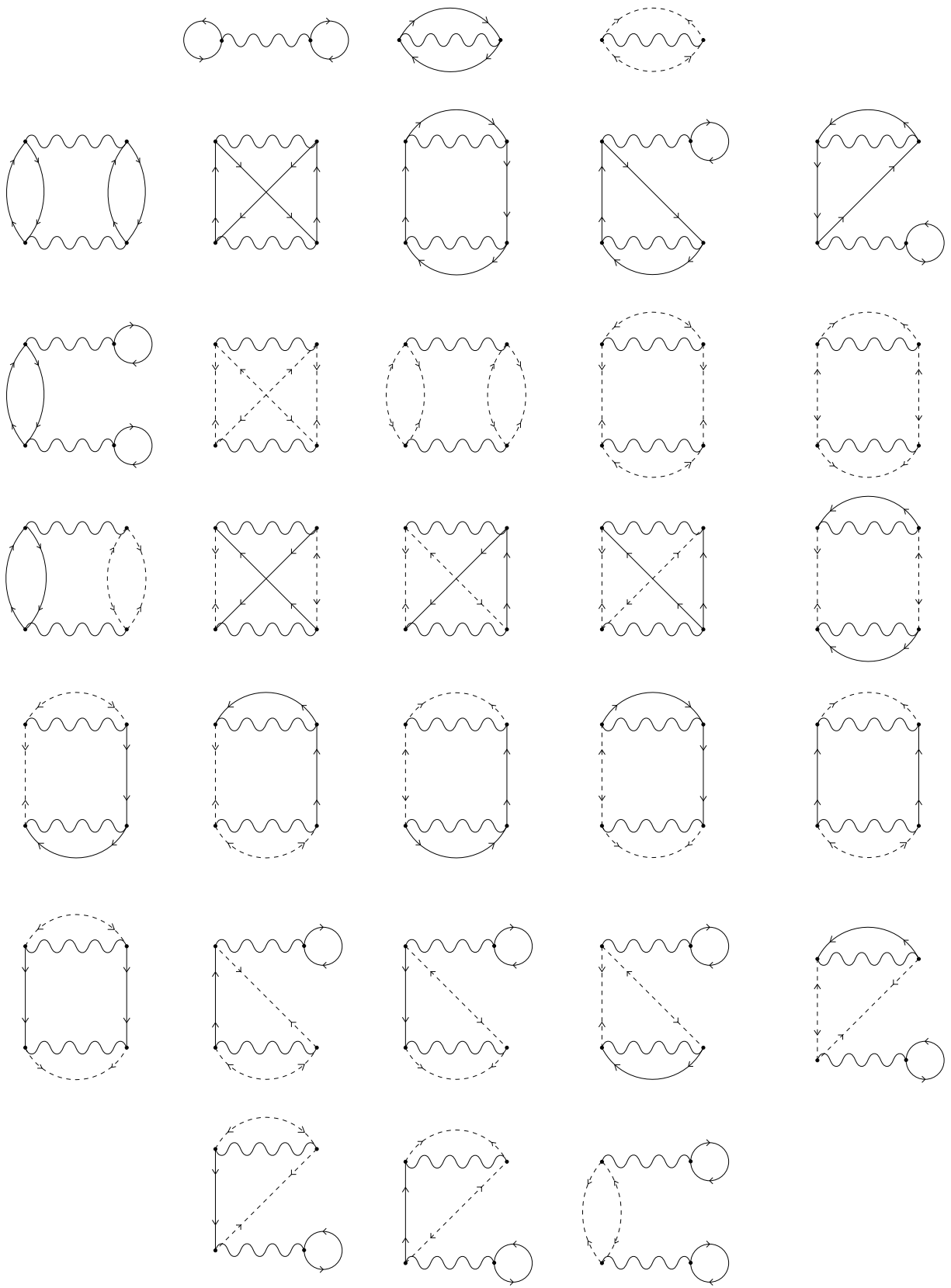


Fig.1: All topologically distinct diagrams up to second order

$$F_d^{(1)} = F \left[\quad \right] = -\frac{\mathcal{V} |V_{\mathbf{q}=0}|^2 \mathcal{V}}{2 \omega_{\mathbf{q}=0}} \left(n^{(0)} \right)^2 \quad (83)$$

where

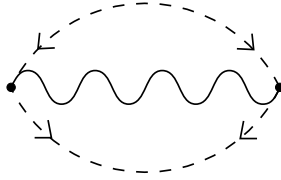
$$n^{(0)} = \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \left(1 - \frac{\epsilon_{\mathbf{k}} - \mu}{R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}}\right) \right) \quad (84)$$

$$R_{\mathbf{k}} = \sqrt{(\epsilon_{\mathbf{k}} - \mu)^2 + |D(\mathbf{k})|^2} \quad (85)$$

and

$$\begin{aligned} F_x^{(1)} &= F \left[\quad \right] \\ &= -\frac{\mathcal{V}}{4} \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \int \frac{d^3 \mathbf{k}'}{(2\pi)^3} \left(\frac{4\pi}{|\mathbf{k} - \mathbf{k}'|^2} + \frac{2\omega_{\mathbf{k}-\mathbf{k}'} |V_{\mathbf{k}-\mathbf{k}'}|^2 \mathcal{V}}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}'})^2 - \omega_{\mathbf{k}-\mathbf{k}'}^2} \right) \\ &\quad \left(1 - \frac{\epsilon_{\mathbf{k}} - \mu}{R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}}\right) \right) \left(1 - \frac{\epsilon_{\mathbf{k}'} - \mu}{R_{\mathbf{k}'}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}'}\right) \right). \end{aligned} \quad (86)$$

In the first contribution, $F_d^{(1)}$, we did not take into account the Coulomb interaction, since this leads to the classical electrostatic energy of the charge distribution and is not included in the **exchange-correlation** part of the free energy. The term involving the anomalous propagators (78), (79)



is also not included in F_{xc} since this term leads to the Hartree part of D_s (i.e. to the second and third terms on the right hand side of eq. (13)).

In order to determine the xc functional D_{xc} in the gap equation (28), the functional derivative of F_{xc} with respect to $\Delta^*(\mathbf{r}, \mathbf{r}')$ needs to be calculated. In the homogeneous case it can be shown that $D_{xc}(\mathbf{k})$, which is the quantity entering the gap equation, is given by

$$D_{xc}(\mathbf{k}) = -\frac{(2\pi)^3 \delta F_{xc}[n, \Delta]}{\mathcal{V} \delta \Delta^*(\mathbf{k})} \quad (87)$$

where $\Delta^*(\mathbf{k})$ is the Fourier transform with respect to $\mathbf{r} - \mathbf{r}'$ of the anomalous density $\Delta^*(\mathbf{r}, \mathbf{r}')$. The calculation of the functional derivative (87) is not straightforward because the perturbative results for F_{xc} given in eqs. (83), (86) represent the xc free energy as a functional of the **potentials**

$$F_{xc} = F_{xc}[\mu, D] \quad (88)$$

and not as a functional of the densities n and Δ . A perturbative analysis similar to the one for the free energy allows one to express the densities as functionals of the potentials:

$$n = n[\mu, D] \quad (89)$$

$$\Delta = \Delta[\mu, D]. \quad (90)$$

$$\mu = \mu[n, \Delta] \quad (91)$$

$$D = D[n, \Delta]. \quad (92)$$

If we knew these functionals then, by insertion into (88), we would have an expression for F_{xc} as a functional of the densities, $F_{xc} = F_{xc}[n, \Delta]$. The inverse functionals (91), (92) are of course not known explicitly. Fortunately, the calculation of $D_{xc}(\mathbf{k})$ does not require the explicit knowledge of the inverse functionals (91), (92). Knowledge of the direct functionals (89) and (90) is sufficient to calculate D_{xc} by means of implicit functional derivatives.

For our calculations we use the zero-order functionals for $n^{(0)}[\mu, D]$ and $\Delta^{(0)}[\mu, D]$, where $n^{(0)}$ is given by (84) and

$$\Delta^{(0)}[\mu, D](\mathbf{k}) = \frac{1}{2} \frac{D(\mathbf{k})}{R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}}\right) \quad (93)$$

Inversion of these functionals leads to functionals for the potentials

$$\mu = \mu[n^{(0)}, \Delta^{(0)}] \quad (94)$$

$$D = D[n^{(0)}, \Delta^{(0)}]. \quad (95)$$

which will then be used as approximations for the exact inverse functionals (91) and (92) by replacement of the zero-order densities by the exact ones. The use of these approximate inverse functionals in the expressions for the first-order free energy will lead to errors of at least second order in the interaction and therefore our theory will be consistent in first order.

By (93) $\Delta^{(0)}(\mathbf{k})$ is expressed as a **function** of μ and $D(\mathbf{k})$ which can be inverted such that

$$D(\mathbf{k}) = G(\mu, \Delta^{(0)}(\mathbf{k})) \quad (96)$$

is a function of μ and $\Delta^{(0)}(\mathbf{k})$. Replacing $\Delta^{(0)}$ by Δ we can then write the normal zero-order density as

$$n^{(0)} = n^{(0)}[\mu, G(\mu, \Delta)] \quad (97)$$

where μ is still a functional of Δ . Since $n^{(0)}$ and $\Delta^{(0)}$ are independent quantities the functional derivative of $n^{(0)}$ with respect to Δ^* must vanish in zeroth order:

$$\frac{\delta n^{(0)}}{\delta \Delta^*(\mathbf{k})} = \frac{\delta n^{(0)}}{\delta \mu} \Big|_{\text{partial}} \frac{\delta \mu}{\delta \Delta^*(\mathbf{k})} + \frac{\delta n^{(0)}}{\delta \Delta^*(\mathbf{k})} \Big|_{\text{partial}} = 0 \quad (98)$$

This equation, together with (93), can be used to calculate

$$\frac{\delta \mu}{\delta \Delta^*(\mathbf{k})} = - \frac{\frac{\delta n^{(0)}}{\delta \Delta^*(\mathbf{k})} \Big|_{\text{partial}}}{\frac{\delta n^{(0)}}{\delta \mu} \Big|_{\text{partial}}} = - \frac{Z_1(\mathbf{k})}{\int d^3 \mathbf{k}_1 Z_0(\mathbf{k}_1)} \quad (99)$$

with the functions

$$Z_0(\mathbf{k}) = \frac{\beta R_{\mathbf{k}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}}\right)}{2 \frac{(\epsilon_{\mathbf{k}} - \mu)^2}{R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}}\right) \cosh^2\left(\frac{\beta}{2} R_{\mathbf{k}}\right) + \beta |G(\mu, \Delta(\mathbf{k}))|^2} \quad (100)$$

$$Z_1(\mathbf{k}) = \frac{(\epsilon_{\mathbf{k}} - \mu)G(\mu, \Delta(\mathbf{k})) \left(\frac{1}{R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2}R_{\mathbf{k}}\right) - \frac{1}{\cosh^2\left(\frac{\beta}{2}R_{\mathbf{k}}\right)} \right)}{\left(\frac{(\epsilon_{\mathbf{k}} - \mu)^2}{R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2}R_{\mathbf{k}}\right) + \frac{|G(\mu, \Delta(\mathbf{k}))|^2 \frac{\beta}{2}}{\cosh^2\left(\frac{\beta}{2}R_{\mathbf{k}}\right)} \right)} \quad (101)$$

and

$$R_{\mathbf{k}} = \sqrt{(\epsilon_{\mathbf{k}} - \mu)^2 + |G(\mu, \Delta(\mathbf{k}))|^2}. \quad (102)$$

We are now able to calculate the xc contributions to the gap equation in first order. The term (83) depends only on the normal density and therefore gives no contribution to the effective pair potential. The other term, eq. (86), is written as

$$F_x^{(1)} = F_x^{(1)}[\mu, G(\mu, \Delta)] \quad (103)$$

and we calculate $D_x^{(1)}$ according to

$$D_x^{(1)}(\mathbf{k}) = \frac{\delta F_x^{(1)}}{\delta \mu} \Big|_{\text{partial}} \frac{\delta \mu}{\delta \Delta^*(\mathbf{k})} + \frac{\delta F_x^{(1)}}{\delta \Delta^*(\mathbf{k})} \Big|_{\text{partial}}. \quad (104)$$

Using (99) we get after a lengthy calculation [14] the correlation contribution to the gap equation as a functional of the densities

$$D_x^{(1)}(\mathbf{k}) = \frac{1}{2}Z_1(\mathbf{k}) \left[\int \frac{d^3\mathbf{k}_1}{(2\pi)^3} w(\mathbf{k}, \mathbf{k}_1) \left(1 - \frac{\epsilon_{\mathbf{k}_1} - \mu}{R_{\mathbf{k}_1}} \tanh\left(\frac{\beta}{2}R_{\mathbf{k}_1}\right) \right) \right. \\ \left. - \frac{\int \frac{d^3\mathbf{k}_1}{(2\pi)^3} \int \frac{d^3\mathbf{k}_2}{(2\pi)^3} Z_0(\mathbf{k}_1) w(\mathbf{k}_1, \mathbf{k}_2) \left(1 - \frac{\epsilon_{\mathbf{k}_2} - \mu}{R_{\mathbf{k}_2}} \tanh\left(\frac{\beta}{2}R_{\mathbf{k}_2}\right) \right)}{\int \frac{d^3\mathbf{k}_1}{(2\pi)^3} Z_0(\mathbf{k}_1)} \right] \quad (105)$$

where

$$w(\mathbf{k}_1, \mathbf{k}_2) = \frac{4\pi}{|\mathbf{k}_1 - \mathbf{k}_2|^2} + \frac{2\omega_{\mathbf{k}_1 - \mathbf{k}_2} |V_{\mathbf{k}_1 - \mathbf{k}_2}|^2 \mathcal{V}}{(\epsilon_{\mathbf{k}_1} - \epsilon_{\mathbf{k}_2})^2 - \omega_{\mathbf{k}_1 - \mathbf{k}_2}^2}. \quad (106)$$

Expressing the densities in terms of the potentials and using the fact that for the homogeneous case

$$G(\mu, \Delta(\mathbf{k})) = D_s(\mathbf{k}) \quad (107)$$

we arrive at the following integral equation for the gap

$$D_s(\mathbf{k}) = D(\mathbf{k}) + \frac{1}{2} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} w(\mathbf{k}, \mathbf{k}') \frac{D_s(\mathbf{k}')}{R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2}R_{\mathbf{k}}\right) + D_x^{(1)}[D_s](\mathbf{k}). \quad (108)$$

So far we have considered only homogeneous systems. In order to apply the described formalism to inhomogeneous systems, we still need to construct an approximation of the free-energy functional or its functional derivative. In normal-state density functional theory the most widely used approximation is the local density approximation (LDA) where the xc-energy functional is approximated by

$$E_{xc}[n] = \int d^3\mathbf{r} e_{xc}^{hom}(n(\mathbf{r})). \quad (109)$$

$$f_{xc}^{hom}[\mu[n, \Delta(\mathbf{k})], D[n, \Delta(\mathbf{k})]] = \frac{1}{\mathcal{V}} F_{xc}^{hom}[\mu[n, \Delta(\mathbf{k})], D[n, \Delta(\mathbf{k})]] \quad (110)$$

is the xc free energy per unit volume of the homogeneous, superconducting electron gas, the LDA for inhomogeneous superconductors is defined by

$$F_{xc}^{LDA}[n(\mathbf{R}), \Delta_W(\mathbf{R}, \mathbf{k})] = \int d^3\mathbf{R} f_{xc}^{hom}[\mu[n, \Delta(\mathbf{k})], D[n, \Delta(\mathbf{k})]] \Big|_{\substack{n=n(\mathbf{R}) \\ \Delta=\Delta_W(\mathbf{R}, \mathbf{k})}}. \quad (111)$$

Here $\Delta_W(\mathbf{R}, \mathbf{k})$ is the Wigner-transform of the anomalous density,

$$\Delta_W(\mathbf{R}, \mathbf{k}) = \int d^3\mathbf{s} e^{i\mathbf{k}\mathbf{s}} \Delta(\mathbf{R} + \frac{\mathbf{s}}{2}, \mathbf{R} - \frac{\mathbf{s}}{2}), \quad (112)$$

where

$$\mathbf{R} = \frac{\mathbf{r} + \mathbf{r}'}{2}, \quad \mathbf{s} = \mathbf{r} - \mathbf{r}'. \quad (113)$$

The inverse transformation is given by

$$\Delta(\mathbf{r}, \mathbf{r}') = \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\mathbf{s}} \Delta_W(\mathbf{R}, \mathbf{k}). \quad (114)$$

With the approximation (111) at hand one can now calculate the xc-pairing potential in LDA

$$D_{xc}^{LDA}(\mathbf{r}, \mathbf{r}') = -\frac{\delta F_{xc}^{LDA}[n, \Delta_W]}{\delta \Delta^*(\mathbf{r}, \mathbf{r}')} = \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\mathbf{s}} D_{xc}^{LDA}(\mathbf{R}, \mathbf{k}). \quad (115)$$

The Wigner transform $D_{xc}^{LDA}(\mathbf{R}, \mathbf{k})$ of $D_{xc}^{LDA}(\mathbf{r}, \mathbf{r}')$ is most conveniently calculated from the identity

$$D_{xc}^{LDA}(\mathbf{R}, \mathbf{k}) = -\frac{(2\pi)^3 \delta F_{xc}^{hom}[\mu[n, \Delta], D[n, \Delta]]}{\mathcal{V} \delta \Delta^*(\mathbf{k})} \Big|_{\substack{n=n(\mathbf{R}) \\ \Delta=\Delta_W(\mathbf{R}, \mathbf{k})}}. \quad (116)$$

With this approximate functional inserted in eq.(13) we then can solve eqs.(7) to (15) until self-consistency is reached or, instead, use

$$D_{xc}^{LDA}(\alpha, \mathbf{k}) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \phi_{\alpha, \mathbf{k}}^*(\mathbf{r}) \phi_{\alpha, \bar{\mathbf{k}}}^*(\mathbf{r}') D_{xc}^{LDA}(\mathbf{r}, \mathbf{r}') \quad (117)$$

to solve the gap equation (28) and perform the self-consistency cycle (17), (26) to (30).

There is still the numerical inconvenience that the inversion (94) and (95) can not be done explicitly, not even in zeroth order, while the expression (94) for the proposed LDA still depends explicitly on the function $\Delta(\mathbf{k})$. We suggest to approximate the zero-order functional $n^{(0)}[\mu, D]$ given by (84) by the zero-order expression for the normal state homogeneous electron gas:

$$n^{(0)} \approx \int \frac{d^3\mathbf{k}}{(2\pi)^3} \left(1 - \tanh\left(\frac{\beta}{2}(\epsilon_{\mathbf{k}} - \mu)\right) \right). \quad (118)$$

$n^{(0)}$ now is only a **function** of μ which can easily be inverted numerically for any given inverse temperature β . Following our prescription we use this function as an approximation for the LDA by inserting the local, inhomogeneous density

$$\mu = \mu(n)|_{n=n(\mathbf{R})}. \quad (119)$$

right hand side of eq. (104).

When using eq.(96) as an approximation to the inverse functional (92) we have to take into account that $G(\mu, \Delta(\mathbf{k}))$ is a function of the **function** $\Delta(\mathbf{k})$ which depends on \mathbf{k} not only through the \mathbf{k} -dependence of $\Delta(\mathbf{k})$ but also via the parameter $\epsilon_{\mathbf{k}} - \mu$. $G(\mu, \Delta(\mathbf{k}))$ is - as well as $\mu(n)$ - known only numerically for each value of β .

Making use of all the described approximations we obtain for the first-order xc contribution to the Wigner transform of the LDA pair potential the expression

$$D_x^{LDA}(\mathbf{R}, \mathbf{k}) = D_x^{(1)}[\mu(n(\mathbf{R}), G(\mu(n(\mathbf{R})), \Delta_W(\mathbf{R}, \mathbf{k})))](\mathbf{R}, \mathbf{k}) \quad (120)$$

where the functional $D_x^{(1)}[\mu, G]$ is given by eq. (105).

6 Spin-Current-Density-Functional Formalism for Superconductors in a Magnetic Field

In this section we present an extension of the basic density functional formalism for superconductors, as described in section 2, to the situation of superconducting systems in the presence of a static external magnetic field [15, 16]. Spin degrees of freedom will be taken into account explicitly. In order to introduce magnetic fields in the basic Hamiltonian, we make the usual minimal substitution

$$\hat{\mathbf{p}} \rightarrow -i\nabla + \frac{1}{c}\mathbf{A}(\mathbf{r}) \quad (121)$$

with $\mathbf{A}(\mathbf{r})$ being the vector potential. For convenience we first consider only magnetic fields with a fixed direction in space. Taking this direction as quantization axis, one can distinguish between spin-up and spin-down densities, n_{\uparrow} and n_{\downarrow} , as well as spin-up and spin-down paramagnetic current densities, $\mathbf{j}_{p\uparrow}$ and $\mathbf{j}_{p\downarrow}$, respectively. For normal (i.e. non-superconducting) systems this procedure was proposed by Vignale and Rasolt [17, 18]. Later in this section we shall describe a formalism allowing the treatment of arbitrary magnetic fields.

We start from the grand-canonical Hamiltonian

$$\begin{aligned} \hat{H} &= \sum_{\sigma=\uparrow\downarrow} \int d^3\mathbf{r} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \hat{\Psi}_{\sigma}(\mathbf{r}) + \hat{U} + \hat{W} + \hat{V} + \hat{A}_1 + \hat{A}_2 \\ &- \iint \left(D^*(\mathbf{r}, \mathbf{r}') \hat{\Psi}_{\uparrow}(\mathbf{r}) \hat{\Psi}_{\downarrow}(\mathbf{r}') + D(\mathbf{r}, \mathbf{r}') \hat{\Psi}_{\downarrow}^{\dagger}(\mathbf{r}') \hat{\Psi}_{\uparrow}^{\dagger}(\mathbf{r}) \right) d^3\mathbf{r} d^3\mathbf{r}' \end{aligned} \quad (122)$$

where \hat{U} and \hat{W} are given by (2) and (3), respectively, and the external potential term

$$\hat{V} = \sum_{\sigma} \int d^3\mathbf{r} \hat{n}_{\sigma}(\mathbf{r}) (v_{\sigma}(\mathbf{r}) - \mu) \quad (123)$$

describes the coupling to the spin densities.

$$\hat{n}_{\sigma}(\mathbf{r}) = \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\Psi}_{\sigma}(\mathbf{r}) \quad \sigma = \uparrow, \downarrow. \quad (124)$$

Eq. (123) can be rewritten as

$$\begin{aligned} \hat{V} &= \int d^3\mathbf{r} (\hat{n}_{\uparrow}(\mathbf{r}) + \hat{n}_{\downarrow}(\mathbf{r})) \left[\frac{1}{2}(v_{\uparrow}(\mathbf{r}) + v_{\downarrow}(\mathbf{r})) - \mu \right] \\ &+ \int d^3\mathbf{r} (\hat{n}_{\uparrow}(\mathbf{r}) - \hat{n}_{\downarrow}(\mathbf{r})) \left[\frac{1}{2}(v_{\uparrow}(\mathbf{r}) - v_{\downarrow}(\mathbf{r})) \right]. \end{aligned} \quad (125)$$

$$v(\mathbf{r}) = \frac{1}{2}(v_{\uparrow}(\mathbf{r}) + v_{\downarrow}(\mathbf{r})) \quad (126)$$

and the Zeeman coupling of the spin magnetization $\hat{\mathbf{m}}(\mathbf{r}) = -\mu_B(\hat{n}_{\uparrow}(\mathbf{r}) - \hat{n}_{\downarrow}(\mathbf{r}))$ to the magnetic field

$$B_z(\mathbf{r}) = c(v_{\uparrow}(\mathbf{r}) - v_{\downarrow}(\mathbf{r})), \quad (127)$$

which has a fixed direction in space (chosen to be the z axis).

The terms containing the vector potential are given by

$$\hat{A}_1 = \frac{1}{c} \sum_{\sigma} \int d^3\mathbf{r} \hat{\mathbf{j}}_{p\sigma}(\mathbf{r}) \mathbf{A}_{\sigma}(\mathbf{r}) \quad (128)$$

and

$$\hat{A}_2 = \frac{1}{2c^2} \sum_{\sigma} \int d^3\mathbf{r} \hat{n}_{\sigma}(\mathbf{r}) \mathbf{A}_{\sigma}^2(\mathbf{r}) \quad (129)$$

where $\hat{\mathbf{j}}_{p\sigma}(\mathbf{r})$ is the paramagnetic spin-current-density operator

$$\hat{\mathbf{j}}_{p\sigma}(\mathbf{r}) = \frac{1}{2i} \left(\hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r})(\nabla\hat{\Psi}_{\sigma}(\mathbf{r})) - (\nabla\hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}))\hat{\Psi}_{\sigma}(\mathbf{r}) \right). \quad (130)$$

As in the spin-current density functional formalism (SCDFT) of Vignale and Rasolt two (unphysical) spin-dependent vector potentials \mathbf{A}_{σ} are introduced here as a formal device. For any real system one has to set $\mathbf{A}_{\downarrow} = \mathbf{A}_{\uparrow} = \mathbf{A}$.

Following the finite-temperature extension [6] of ordinary density functional theory, it is straightforward to establish the existence of a 1-1 mapping of the set of potentials $\{v_{\sigma}(\mathbf{r}) - \mu, \mathbf{A}_{\sigma}(\mathbf{r}), D(\mathbf{r}, \mathbf{r}')\}$ onto the set of equilibrium densities $\{n_{\sigma}(\mathbf{r}), \mathbf{j}_{p\sigma}(\mathbf{r}), \Delta(\mathbf{r}, \mathbf{r}')\}$ where the anomalous density $\Delta(\mathbf{r}, \mathbf{r}')$ is defined by eq. (5). As a consequence, the grand canonical potential can be written as a density functional which is minimized by the equilibrium densities of the particular system considered.

As usual this variational principle can be used to construct the Hamiltonian of a non-interacting system yielding the same densities as the interacting system. This Hamiltonian is given by

$$\begin{aligned} H_s &= \int d^3\mathbf{r} \sum_{\sigma} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(\frac{1}{2} \left(-i\nabla + \frac{1}{c} A_{s\sigma}(\mathbf{r}) \right)^2 + v_{s\sigma}(\mathbf{r}) - \mu \right) \hat{\Psi}_{\sigma}(\mathbf{r}) \\ &- \int d^3\mathbf{r} \int d^3\mathbf{r}' (D_s^*(\mathbf{r}, \mathbf{r}') \hat{\Delta}(\mathbf{r}, \mathbf{r}') + H.c.). \end{aligned} \quad (131)$$

It can be diagonalized by the generalized Bogoliubov transformation

$$\hat{\Psi}_{\sigma}(\mathbf{r}) = \sum_k \sum_{\tau} \left(u_{\sigma k\tau}(\mathbf{r}) \hat{\gamma}_{k\tau} + v_{\sigma k\tau}^*(\mathbf{r}) \hat{\gamma}_{k\tau}^{\dagger} \right). \quad (132)$$

The transformation is required to be unitary (i.e. to conserve the norm) and canonical (i.e. to conserve the anticommutation relations of the field operators $\hat{\Psi}$). This imposes certain conditions on the particle and hole amplitudes $u_{\sigma k\tau}(\mathbf{r})$ and $v_{\sigma k\tau}(\mathbf{r})$. Unitarity requires that

$$\int d^3\mathbf{r} \sum_{\sigma} (u_{\sigma k\tau}(\mathbf{r}) u_{\sigma k'\tau'}^*(\mathbf{r}) + v_{\sigma k\tau}(\mathbf{r}) v_{\sigma k'\tau'}^*(\mathbf{r})) = \delta_{k,k'} \delta_{\tau,\tau'} \quad (133)$$

while the conditions

$$\sum_{k\tau} (u_{\sigma k\tau}(\mathbf{r})v_{\sigma'k\tau}^*(\mathbf{r}') + v_{\sigma k\tau}^*(\mathbf{r})u_{\sigma'k\tau}(\mathbf{r}')) = 0 \quad (135)$$

and

$$\sum_{k\tau} (u_{\sigma k\tau}^*(\mathbf{r})u_{\sigma'k\tau}(\mathbf{r}') + v_{\sigma k\tau}(\mathbf{r})v_{\sigma'k\tau}^*(\mathbf{r}')) = \delta_{\sigma\sigma'}\delta(\mathbf{r}-\mathbf{r}') \quad (136)$$

ensure that the transformation is canonical. These equations can also be regarded as orthonormality and completeness relations, respectively.

The Hamiltonian (131) is diagonalized by the Bogoliubov transformation (132) if $u_{\sigma k\tau}(\mathbf{r})$ and $v_{\sigma k\tau}(\mathbf{r})$ are solutions of the eigenvalue equations

$$h_{\uparrow}u_{\uparrow k\tau}(\mathbf{r}) + \int d^3\mathbf{r}' D_s(\mathbf{r}, \mathbf{r}')v_{\downarrow k\tau}(\mathbf{r}') = E_{k\tau}u_{\uparrow k\tau}(\mathbf{r}) \quad (137)$$

$$-h_{\downarrow}^*v_{\downarrow k\tau}(\mathbf{r}) + \int d^3\mathbf{r}' D_s^*(\mathbf{r}', \mathbf{r})u_{\uparrow k\tau}(\mathbf{r}') = E_{k\tau}v_{\downarrow k\tau}(\mathbf{r}) \quad (138)$$

$$-h_{\uparrow}^*v_{\uparrow k\tau}(\mathbf{r}) - \int d^3\mathbf{r}' D_s^*(\mathbf{r}, \mathbf{r}')u_{\downarrow k\tau}(\mathbf{r}') = E_{k\tau}v_{\uparrow k\tau}(\mathbf{r}) \quad (139)$$

$$h_{\downarrow}u_{\downarrow k\tau}(\mathbf{r}) - \int d^3\mathbf{r}' D_s(\mathbf{r}', \mathbf{r})v_{\uparrow k\tau}(\mathbf{r}') = E_{k\tau}u_{\downarrow k\tau}(\mathbf{r}) \quad (140)$$

where

$$h_{\sigma} = \frac{1}{2} \left(-i\nabla + \frac{1}{c}\mathbf{A}_{s\sigma}(\mathbf{r}) \right)^2 + v_{s\sigma}(\mathbf{r}) - \mu. \quad (141)$$

and h_{σ}^* is the complex conjugate of h_{σ} (not the Hermitian conjugate). The densities can be expressed in terms of the $u_{\sigma k\tau}(\mathbf{r})$ and $v_{\sigma k\tau}(\mathbf{r})$ as

$$n_{\sigma}(\mathbf{r}) = \sum_{k\tau} (|u_{\sigma k\tau}(\mathbf{r})|^2 f_{\beta}(E_{k\tau}) + |v_{\sigma k\tau}(\mathbf{r})|^2 f_{\beta}(-E_{k\tau})) \quad (142)$$

$$\Delta(\mathbf{r}, \mathbf{r}') = \sum_{k\tau} \left(u_{\uparrow k\tau}(\mathbf{r})v_{\downarrow k\tau}^*(\mathbf{r}') f_{\beta}(-E_{k\tau}) + v_{\uparrow k\tau}^*(\mathbf{r})u_{\downarrow k\tau}(\mathbf{r}') f_{\beta}(E_{k\tau}) \right) \quad (143)$$

$$\begin{aligned} \mathbf{j}_{p\sigma}(\mathbf{r}) &= \frac{1}{2i} \sum_{k\tau} [(u_{\sigma k\tau}^*(\mathbf{r})\nabla u_{\sigma k\tau}(\mathbf{r}) - (\nabla u_{\sigma k\tau}^*(\mathbf{r}))u_{\sigma k\tau}(\mathbf{r})) f_{\beta}(E_{k\tau}) \\ &\quad + (v_{\sigma k\tau}^*(\mathbf{r})\nabla v_{\sigma k\tau}(\mathbf{r}) - (\nabla v_{\sigma k\tau}^*(\mathbf{r}))v_{\sigma k\tau}(\mathbf{r})) f_{\beta}(-E_{k\tau})] \end{aligned} \quad (144)$$

where $f_{\beta}(E)$ is the Fermi distribution (11). The effective single-particle potentials are determined by the relations

$$\begin{aligned} v_{s\sigma}(\mathbf{r}) &= v_{\sigma}(\mathbf{r}) + \int d^3\mathbf{r}' \sum_{\sigma'} \frac{n_{\sigma'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &\quad + \frac{1}{2c^2} (\mathbf{A}_{\sigma}^2(\mathbf{r}) - (\mathbf{A}_{\sigma}(\mathbf{r}) + \mathbf{A}_{xc\sigma}(\mathbf{r}))^2) + v_{xc}[n_{\sigma}, \mathbf{j}_{p\sigma}, \Delta](\mathbf{r}) \end{aligned} \quad (145)$$

$$D_s(\mathbf{r}, \mathbf{r}') = D(\mathbf{r}, \mathbf{r}') - \int d^3\mathbf{x} \int d^3\mathbf{x}' \tilde{w}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Delta(\mathbf{x}', \mathbf{x}) + D_{xc}[n_{\sigma}, \mathbf{j}_{p\sigma}, \Delta](\mathbf{r}, \mathbf{r}') \quad (146)$$

where w , as defined in eq. (36), includes the phonon-induced interactions. The xc potentials are, as usual, defined as functional derivatives of an xc-free-energy functional:

$$v_{xc\sigma}[n_\sigma, \mathbf{j}_{p\sigma}, \Delta](\mathbf{r}) = \frac{\delta F_{xc}^\beta[n_\sigma, \mathbf{j}_{p\sigma}, \Delta]}{\delta n_\sigma(\mathbf{r})} \quad (148)$$

$$D_{xc}[n_\sigma, \mathbf{j}_{p\sigma}, \Delta](\mathbf{r}, \mathbf{r}') = -\frac{\delta F_{xc}^\beta[n_\sigma, \mathbf{j}_{p\sigma}, \Delta]}{\delta \Delta^*(\mathbf{r}, \mathbf{r}')} \quad (149)$$

$$\mathbf{A}_{xc\sigma}[n_\sigma, \mathbf{j}_{p\sigma}, \Delta](\mathbf{r}) = c \frac{\delta F_{xc}^\beta[n_\sigma, \mathbf{j}_{p\sigma}, \Delta]}{\delta \mathbf{j}_{p\sigma}(\mathbf{r})}. \quad (150)$$

The grand canonical potential is then given by

$$\begin{aligned} \Omega = & \Omega_s - \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3\mathbf{r} \sum_{\sigma} n_\sigma(\mathbf{r}) v_{xc\sigma}(\mathbf{r}) \\ & - \int d^3\mathbf{r} \int d^3\mathbf{r}' \int d^3\mathbf{x} \int d^3\mathbf{x}' \Delta^*(\mathbf{r}, \mathbf{r}') \tilde{w}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Delta(\mathbf{x}', \mathbf{x}) \\ & - \frac{1}{c} \int d^3\mathbf{r} \sum_{\sigma} \mathbf{j}_{p\sigma}(\mathbf{r}) \mathbf{A}_{xc\sigma}(\mathbf{r}) + \int d^3\mathbf{r} \int d^3\mathbf{r}' [D_{xc}^*(\mathbf{r}, \mathbf{r}') \Delta(\mathbf{r}', \mathbf{r}) + c.c.] \\ & + \frac{1}{8\pi} \int d^3\mathbf{r} B^2(\mathbf{r}) + F_{xc}[n_\sigma, \mathbf{j}_{p\sigma}, \Delta]. \end{aligned} \quad (151)$$

The quadratic term in \mathbf{B} represents the energy contribution of the magnetic field. In the $T = 0$ case, eq. (151) reduces to the ground state energy.

For both normal and superconducting systems, the formalism presented so far has several drawbacks: (i) The analysis is restricted to magnetic fields with a fixed direction in space. (ii) Unphysical spin-dependent vector potentials have to be introduced. (iii) The potentials $v_\sigma(\mathbf{r})$ and $\mathbf{A}_\sigma(\mathbf{r})$ are treated as independent quantities. In any real system, however, the magnetic field given by eq. (127) must be equal to the curl of the vector potential, i.e. $v_\sigma(\mathbf{r})$ and $\mathbf{A}_\sigma(\mathbf{r})$ are *not* independent.

In the following we will present an alternative, though similar formalism which does not have these drawbacks. This formalism is presented here in a superconducting context although it can be used for *normal* systems in magnetic fields as well [16]. In this case it represents a (possibly simpler) alternative to Vignale and Rasolt's SCDFT for arbitrary field directions.

To this end, the external potential term (125) is generalized to

$$\hat{V} = \int d^3\mathbf{r} \hat{n}(\mathbf{r})(v(\mathbf{r}) - \mu) - \int d^3\mathbf{r} \hat{\mathbf{m}}(\mathbf{r}) \mathbf{B}(\mathbf{r}). \quad (152)$$

where

$$\hat{\mathbf{m}}(\mathbf{r}) = -\mu_B \sum_{\alpha\beta} \hat{\Psi}_\alpha^\dagger(\mathbf{r}) \boldsymbol{\sigma}_{\alpha\beta} \hat{\Psi}_\beta(\mathbf{r}) \quad (153)$$

is the spin-magnetization-density operator. $\boldsymbol{\sigma}_{\alpha\beta}$ denotes the vector of Pauli spin matrices and μ_B is the Bohr magneton. \mathbf{B} and \mathbf{m} can have arbitrary directions.

The full Hamiltonian of our system is then

$$\begin{aligned} \hat{H} = & \sum_{\sigma=\uparrow\downarrow} \int d^3\mathbf{r} \hat{\Psi}_\sigma^\dagger(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \hat{\Psi}_\sigma(\mathbf{r}) + \hat{U} + \hat{W} + \hat{V} + \hat{A}_1 + \hat{A}_2 \\ & - \iint \left(D^*(\mathbf{r}, \mathbf{r}') \hat{\Psi}_\uparrow(\mathbf{r}) \hat{\Psi}_\downarrow(\mathbf{r}') + D(\mathbf{r}, \mathbf{r}') \hat{\Psi}_\downarrow^\dagger(\mathbf{r}') \hat{\Psi}_\uparrow^\dagger(\mathbf{r}) \right) d^3\mathbf{r} d^3\mathbf{r}'. \end{aligned} \quad (154)$$

$$\hat{A}_1 = \frac{1}{c} \int d^3\mathbf{r} \hat{\mathbf{j}}_p(\mathbf{r}) \mathbf{A}(\mathbf{r}) \quad (155)$$

with $\hat{\mathbf{j}}_p(\mathbf{r}) = \sum_{\sigma} \hat{\mathbf{j}}_{p\sigma}(\mathbf{r})$, and

$$\hat{A}_2 = \frac{1}{2c^2} \int d^3\mathbf{r} \hat{n}(\mathbf{r}) \mathbf{A}^2(\mathbf{r}). \quad (156)$$

We now add the magnetization current to the paramagnetic current

$$\hat{\mathbf{j}}_m(\mathbf{r}) := \hat{\mathbf{j}}_p(\mathbf{r}) - c \nabla \times \hat{\mathbf{m}}(\mathbf{r}). \quad (157)$$

With this definition, and using $\mathbf{B}(\mathbf{r}) = \nabla \times \mathbf{A}(\mathbf{r})$, we can rewrite $(\hat{V} + \hat{A}_1)$ as

$$\hat{V} + \hat{A}_1 = \int d^3\mathbf{r} \hat{n}(\mathbf{r}) (v(\mathbf{r}) - \mu) + \frac{1}{c} \int d^3\mathbf{r} \hat{\mathbf{j}}_m(\mathbf{r}) \mathbf{A}(\mathbf{r}) \quad (158)$$

provided that either the vector potential or the magnetization density falls off rapidly enough for large r to ensure the validity of Gauss' theorem.

In order to construct a density functional formalism based on the Hamiltonian (154) one shows, as usual, the existence of a 1-1 mapping from the set of potentials $\{v(\mathbf{r}) - \mu, \mathbf{A}(\mathbf{r}), D(\mathbf{r}, \mathbf{r}')\}$ onto the set of densities $\{n(\mathbf{r}), \mathbf{j}_m(\mathbf{r}), \Delta(\mathbf{r}, \mathbf{r}')\}$.

The Hamiltonian of the non-interacting system yielding the same densities as (154) can be written as

$$H_s = \int d^3\mathbf{r} \sum_{\sigma} \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) \left(-\frac{\nabla^2}{2} + \frac{1}{2c^2} A_s^2(\mathbf{r}) + v_s(\mathbf{r}) - \mu \right) \hat{\Psi}_{\sigma}(\mathbf{r}) + \quad (159)$$

$$+ \frac{1}{c} \int d^3\mathbf{r} \mathbf{A}_s(\mathbf{r}) \hat{\mathbf{j}}_m(\mathbf{r}) - \int d^3\mathbf{r} \int d^3\mathbf{r}' (D_s^*(\mathbf{r}, \mathbf{r}') \hat{\Delta}(\mathbf{r}, \mathbf{r}') + H.c.).$$

and can also be diagonalized by the Bogoliubov transformation (132). The resulting eigenvalue equations are conveniently expressed in matrix form:

$$\hat{M} \begin{pmatrix} u_{\uparrow k\tau}(\mathbf{r}) \\ v_{\downarrow k\tau}(\mathbf{r}) \\ v_{\uparrow k\tau}(\mathbf{r}) \\ u_{\downarrow k\tau}(\mathbf{r}) \end{pmatrix} = E_{k\tau} \begin{pmatrix} u_{\uparrow k\tau}(\mathbf{r}) \\ v_{\downarrow k\tau}(\mathbf{r}) \\ v_{\uparrow k\tau}(\mathbf{r}) \\ u_{\downarrow k\tau}(\mathbf{r}) \end{pmatrix} \quad (160)$$

where the matrix \hat{M} is given by

$$\begin{pmatrix} h + \mu_B \mathbf{B}_s \cdot \boldsymbol{\sigma}_{\uparrow\uparrow} & \hat{D}_s(\mathbf{r}, \mathbf{r}') & 0 & \mu_B \mathbf{B}_s \cdot \boldsymbol{\sigma}_{\uparrow\downarrow} \\ \hat{D}_s^*(\mathbf{r}', \mathbf{r}) & -h^* - \mu_B \mathbf{B}_s \cdot \boldsymbol{\sigma}_{\downarrow\downarrow}^* & -\mu_B \mathbf{B}_s \cdot \boldsymbol{\sigma}_{\downarrow\uparrow}^* & 0 \\ 0 & -\mu_B \mathbf{B}_s \cdot \boldsymbol{\sigma}_{\uparrow\downarrow}^* & -h^* - \mu_B \mathbf{B}_s \cdot \boldsymbol{\sigma}_{\uparrow\uparrow}^* & -\hat{D}_s^*(\mathbf{r}, \mathbf{r}') \\ \mu_B \mathbf{B}_s \cdot \boldsymbol{\sigma}_{\downarrow\uparrow} & 0 & -\hat{D}_s(\mathbf{r}', \mathbf{r}) & h + \mu_B \mathbf{B}_s \cdot \boldsymbol{\sigma}_{\downarrow\downarrow} \end{pmatrix} \quad (161)$$

Here

$$h = \frac{1}{2} (-i\nabla + \frac{1}{c} \mathbf{A}_s(\mathbf{r}))^2 + v_s(\mathbf{r}) - \mu \quad (162)$$

and $\hat{D}_s(\mathbf{r}, \mathbf{r}')$ is a shorthand notation for the integral operator $\int D_s(\mathbf{r}, \mathbf{r}') \dots d^3\mathbf{r}'$. \mathbf{B}_s is given by

$$\mathbf{B}_s(\mathbf{r}) = \nabla \times \mathbf{A}_s(\mathbf{r}). \quad (163)$$

$$n(\mathbf{r}) = \sum_{\sigma} \sum_{k\tau} [|u_{\sigma k\tau}(\mathbf{r})|^2 f_{\beta}(E_{k\tau}) + |v_{\sigma k\tau}(\mathbf{r})|^2 f_{\beta}(-E_{k\tau})] \quad (164)$$

$$\Delta(\mathbf{r}, \mathbf{r}') = \sum_{k\tau} \left[u_{\uparrow k\tau}(\mathbf{r}) v_{\downarrow k\tau}^*(\mathbf{r}') f_{\beta}(-E_{k\tau}) + v_{\uparrow k\tau}^*(\mathbf{r}) u_{\downarrow k\tau}(\mathbf{r}') f_{\beta}(E_{k\tau}) \right] \quad (165)$$

$$\mathbf{j}_m(\mathbf{r}) = \mathbf{j}_p - c\mu_B \nabla \times \sum_{\mu\nu} \sum_{k\tau} \left[u_{\mu k\tau}^*(\mathbf{r}) \sigma_{\mu\nu} u_{\nu k\tau}(\mathbf{r}) f_{\beta}(E_{k\tau}) + v_{\mu k\tau}(\mathbf{r}) \sigma_{\mu\nu} v_{\nu k\tau}^*(\mathbf{r}) f_{\beta}(-E_{k\tau}) \right] \quad (166)$$

with

$$\mathbf{j}_p(\mathbf{r}) = \frac{1}{2i} \sum_{\sigma} \sum_{k\tau} \left[[u_{\sigma k\tau}^*(\mathbf{r}) \nabla u_{\sigma k\tau}(\mathbf{r}) - (\nabla u_{\sigma k\tau}^*(\mathbf{r})) u_{\sigma k\tau}(\mathbf{r})] f_{\beta}(E_{k\tau}) + \right. \quad (167) \\ \left. + [v_{\sigma k\tau}^*(\mathbf{r}) \nabla v_{\sigma k\tau}(\mathbf{r}) - (\nabla v_{\sigma k\tau}^*(\mathbf{r})) v_{\sigma k\tau}(\mathbf{r})] f_{\beta}(-E_{k\tau}) \right]$$

The effective single-particle potentials are determined with the use of the variational principle, yielding

$$v_s(\mathbf{r}) = v(\mathbf{r}) + \int d^3 \mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{1}{2c^2} (\mathbf{A}^2(\mathbf{r}) - (\mathbf{A}(\mathbf{r}) + \mathbf{A}_{xc}(\mathbf{r}))^2) + v_{xc}[n, \mathbf{j}_m, \Delta](\mathbf{r}) \quad (168)$$

$$D_s(\mathbf{r}, \mathbf{r}') = D(\mathbf{r}, \mathbf{r}') - \int d^3 \mathbf{x} \int d^3 \mathbf{x}' \tilde{w}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Delta(\mathbf{x}', \mathbf{x}) + D_{xc}[n, \mathbf{j}_m, \Delta](\mathbf{r}, \mathbf{r}') \quad (169)$$

$$\mathbf{A}_s(\mathbf{r}) = \mathbf{A}(\mathbf{r}) + \mathbf{A}_{xc}[n, \mathbf{j}_m, \Delta](\mathbf{r}) \quad (170)$$

where the xc potentials are again defined as functional derivatives of the xc-free-energy functional $F_{xc}^{\beta}[n, \mathbf{j}_m, \Delta]$ with respect to the corresponding densities.

For the special case of a local pairing potential the requirement of gauge invariance can be used to demonstrate that F_{xc} can depend only on n , $|\Delta|$ and $\nabla \times \left(\frac{\mathbf{j}_m}{n} \right)$:

$$F_{xc}[n, \Delta, \mathbf{j}_m] = \tilde{F}_{xc}[n, |\Delta|, \nabla \times \left(\frac{\mathbf{j}_m}{n} \right)] \quad (171)$$

This equation can serve as a constraint for the construction of approximate functionals.

Self-consistent calculations on the basis of the above KS type equations can be performed as usual. The presence of the magnetic field, however, introduces an additional complication. The induced currents give rise to a vector potential, which adds to the external vector potential according to

$$\mathbf{A}(\mathbf{r}) = \mathbf{A}_{ext}(\mathbf{r}) + \mathbf{A}_{ind}(\mathbf{r}). \quad (172)$$

To include this effect one first makes an initial guess for $\mathbf{A}_{ind}(\mathbf{r})$ and uses $\mathbf{A}(\mathbf{r})$ from eq. (172) as external vector potential in the self-consistent equations (160)-(170). These lead to the physical current density

$$\mathbf{j}(\mathbf{r}) = \mathbf{j}_m(\mathbf{r}) + \frac{1}{c} n(\mathbf{r}) \mathbf{A}(\mathbf{r}) \quad (173)$$

which is used to calculate the new $\mathbf{A}_{ind}(\mathbf{r})$ from the Maxwell equation

$$\nabla \times \nabla \times \mathbf{A}_{ind}(\mathbf{r}) = -\frac{4\pi}{c} \mathbf{j}(\mathbf{r}). \quad (174)$$

The new $\mathbf{A}_{ind}(\mathbf{r})$ is used as an input for the next cycle. This procedure is repeated until self-consistency is achieved for both, the densities *and* the vector potential.

Possible applications of the two formalisms described in this section are high-temperature superconductors in magnetic fields and heavy fermion superconductors.

In many cases, experimental data such as the photoabsorption cross-section or the dielectric function are related to the linear response of a system. In this section we will present a density functional scheme for calculating the frequency-dependent linear response of superconductors. The method is analogous to the scheme for normal systems presented in this volume in the chapter on time-dependent density functional theory.

The superconducting state, as described in section 2, is characterized by the normal and the anomalous density. External vector potentials and induced currents are not considered in this section. The Hamiltonian (1) of the system contains three external potentials², which couple to the density operators as follows:

$$\begin{aligned} v(\mathbf{r}) & : & \hat{n}(\mathbf{r}) & := & \sum_{\sigma} \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \\ D^*(\mathbf{r}, \mathbf{r}') & : & \hat{\Delta}(\mathbf{r}, \mathbf{r}') & := & \hat{\psi}_{\uparrow}(\mathbf{r}) \hat{\psi}_{\downarrow}(\mathbf{r}') \\ D(\mathbf{r}, \mathbf{r}') & : & \hat{\Delta}^{\dagger}(\mathbf{r}, \mathbf{r}') & := & \hat{\psi}_{\downarrow}^{\dagger}(\mathbf{r}') \hat{\psi}_{\uparrow}^{\dagger}(\mathbf{r}) \end{aligned} \quad (175)$$

Since a perturbation added to any of these potentials can affect all three densities, we have to define nine response functions. The linear response of the normal density, for instance, is given by:

$$\begin{aligned} n_1(\mathbf{r}, t) & = \int d^3 \mathbf{x} \int dt' \chi(\mathbf{r}, \mathbf{x}; t - t') v_1(\mathbf{x}; t') \\ & + \int d^3 \mathbf{x} \int d^3 \mathbf{x}' \int dt' \Lambda^*(\mathbf{r}, \mathbf{x}, \mathbf{x}'; t - t') D_1(\mathbf{x}, \mathbf{x}'; t') \\ & + \int d^3 \mathbf{x} \int d^3 \mathbf{x}' \int dt' \Lambda(\mathbf{r}, \mathbf{x}, \mathbf{x}'; t - t') D_1^*(\mathbf{x}, \mathbf{x}'; t'), \end{aligned} \quad (176)$$

where v_1 and D_1 are external time-dependent perturbations.

From now on we will use a symbolic notation where the response functions are written as formal integral operators. With this convention the full system of response equations reads:

$$\begin{aligned} n_1 & = \chi v_1 + \Lambda^* D_1 + \Lambda D_1^*, \\ \Delta_1 & = \Gamma v_1 + \Xi D_1 + \tilde{\Xi} D_1^*, \\ \Delta_1^* & = \Gamma^* v_1 + \tilde{\Xi}^* D_1 + \Xi^* D_1^*. \end{aligned} \quad (177)$$

To further simplify the notation we introduce a vector of density responses and a vector of external perturbations.

$$\vec{n}_1 := \begin{pmatrix} n_1 \\ \Delta_1 \\ \Delta_1^* \end{pmatrix}, \quad \vec{v}_1 := \begin{pmatrix} v_1 \\ D_1 \\ D_1^* \end{pmatrix}. \quad (178)$$

With these conventions, the response equations can be written as

$$\vec{n}_1 = \hat{\chi} \vec{v}_1, \quad (179)$$

where $\hat{\chi}$ represents the 3×3 matrix of response operators

$$\hat{\chi} := \begin{pmatrix} \chi & \Lambda^* & \Lambda \\ \Gamma & \Xi & \tilde{\Xi} \\ \Gamma^* & \tilde{\Xi}^* & \Xi^* \end{pmatrix}. \quad (180)$$

²There are three independent *real* functions: $v(\mathbf{r})$, $\text{Re}[D(\mathbf{r}, \mathbf{r}')]$ and $\text{Im}[D(\mathbf{r}, \mathbf{r}')]$. In the present context, however, it is more convenient to use $v(\mathbf{r})$, $D(\mathbf{r}, \mathbf{r}')$ and $D^*(\mathbf{r}, \mathbf{r}')$ instead.

$$\chi(\mathbf{r}, \mathbf{x}; t - t') = -i \left\langle [\hat{n}_H(\mathbf{r}, t), \hat{n}_H(\mathbf{x}, t')] \right\rangle, \quad (181)$$

$$\Lambda(\mathbf{r}, \mathbf{x}, \mathbf{x}'; t - t') = -i \left\langle [\hat{n}_H(\mathbf{r}, t), \hat{\Delta}_H(\mathbf{x}, \mathbf{x}', t')] \right\rangle, \quad (182)$$

$$\Gamma(\mathbf{r}, \mathbf{r}', \mathbf{x}; t - t') = -i \left\langle [\hat{\Delta}_H(\mathbf{r}, \mathbf{r}'; t), \hat{n}_H(\mathbf{x}; t')] \right\rangle, \quad (183)$$

$$\Xi(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; t - t') = -i \left\langle [\hat{\Delta}_H(\mathbf{r}, \mathbf{r}'; t), \hat{\Delta}_H^\dagger(\mathbf{x}, \mathbf{x}'; t')] \right\rangle, \quad (184)$$

$$\tilde{\Xi}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; t - t') = -i \left\langle [\hat{\Delta}_H(\mathbf{r}, \mathbf{r}'; t), \hat{\Delta}_H(\mathbf{x}, \mathbf{x}'; t')] \right\rangle, \quad (185)$$

where the index H denotes operators in the real-time Heisenberg picture.

The unperturbed superconducting system is assumed to be in thermal equilibrium, i.e. $\langle \dots \rangle$ denotes a grand canonical ensemble average over the eigenstates of the full interacting Hamiltonian (1). The full response functions (181) - (185) of the interacting system are very hard to calculate. On the other hand, the corresponding response functions $\hat{\chi}_s$ of the (non-interacting) Kohn-Sham system defined by eqs. (7) - (16) are easily expressed in terms of the particle and hole amplitudes, $u_k(\mathbf{r})$ and $v_k(\mathbf{r})$, respectively. Explicit expressions for the 9 response functions are given in the appendix.

We now define a 3×3 matrix of xc kernels \hat{f}_{xc} by the Dyson-type equation

$$\hat{\chi} = \hat{\chi}_s + \hat{\chi}_s (\hat{w} + \hat{f}_{xc}) \hat{\chi}, \quad (186)$$

where \hat{w} is given by

$$\hat{w} = \begin{pmatrix} u & 0 & 0 \\ 0 & -\tilde{w} & 0 \\ 0 & 0 & -\tilde{w}^* \end{pmatrix}. \quad (187)$$

In (187) u represents the Coulomb interaction while \tilde{w} , as defined in eq. (56), is the sum of the Coulomb and the phonon-induced interactions. Inserting (186) in the response equation (179), one obtains

$$\vec{n}_1 = \hat{\chi}_s (\vec{v}_1 + (\hat{w} + \hat{f}_{xc}) \vec{n}_1). \quad (188)$$

Given an approximation for the xc kernels \hat{f}_{xc} , eq. (188) can be solved numerically by iteration. If the unperturbed system is homogeneous, eq. (188) can even be solved analytically if the effective interaction $(\hat{w} + \hat{f}_{xc})$ is assumed to consist of separable terms only [19].

In the static limit, the Hohenberg-Kohn-Sham formalism developed in section 2 implies that the xc-kernels can be written as

$$\hat{f}_{xc} = \begin{pmatrix} \frac{\delta v_{xc}}{\delta n} & \frac{\delta v_{xc}}{\delta \Delta} & \frac{\delta v_{xc}}{\delta \Delta^*} \\ \frac{\delta D_{xc}}{\delta n} & \frac{\delta D_{xc}}{\delta \Delta} & \frac{\delta D_{xc}}{\delta \Delta^*} \\ \frac{\delta D_{xc}^*}{\delta n} & \frac{\delta D_{xc}^*}{\delta \Delta} & \frac{\delta D_{xc}^*}{\delta \Delta^*} \end{pmatrix}. \quad (189)$$

For eq. (189) to be valid in the case of time-dependent perturbations a time-dependent extension of the density functional theory for superconductors is required. In particular a Runge-Gross theorem as described in this volume in the chapter on time-dependent density functional theory has to be established for superconductors. A theorem of this kind was recently proposed by Wacker, Kümmel and Gross [20]. However, the densities used in this

present, eq. (188) is to be regarded as a potential in the time-dependent case. Eq. (188) can be viewed as the superconducting analogue of the density-functional response scheme described in this volume in the chapter on time-dependent density functional theory. In view of the great success this method has had for normal systems, we expect eq. (188) to be a very efficient tool for calculating the linear response of superconductors. As a first shot, the xc-kernel \hat{f}_{xc} can be approximated by eq. (189) using the static LDA-type xc potentials derived in section 5.

Appendix

In order to calculate the response functions of the Kohn-Sham system we first define the spectral densities $S_{AB}(\omega)$ by

$$S_{AB}(\omega) = \int d(t-t') e^{i\omega(t-t')} \left\langle [\hat{A}(t)_H, \hat{B}(t')_H] \right\rangle_S \quad (\text{A } 1)$$

where $\langle \dots \rangle_S$ denotes a grand canonical ensemble average over the eigenstates of the (non-interacting) Kohn-Sham system (7) - (15). In terms of these spectral densities, the KS response functions can be written as

$$\chi_s(\mathbf{r}, \mathbf{x}; \omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{nn}(\mathbf{r}, \mathbf{x}; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 2)$$

$$\Lambda_s(\mathbf{r}, \mathbf{x}, \mathbf{x}'; \omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{n\Delta}(\mathbf{r}, \mathbf{x}, \mathbf{x}'; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 3)$$

$$\Lambda_s^*(\mathbf{r}, \mathbf{x}, \mathbf{x}'; -\omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{n\Delta^\dagger}(\mathbf{r}, \mathbf{x}, \mathbf{x}'; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 4)$$

$$\Gamma_s(\mathbf{r}, \mathbf{r}', \mathbf{x}; \omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{\Delta n}(\mathbf{r}, \mathbf{r}', \mathbf{x}; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 5)$$

$$\Gamma_s^*(\mathbf{r}, \mathbf{r}', \mathbf{x}, -\omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{\Delta^\dagger n}(\mathbf{r}, \mathbf{r}', \mathbf{x}; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 6)$$

$$\Xi_s(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; \omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{\Delta\Delta^\dagger}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 7)$$

$$\tilde{\Xi}_s(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; \omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{\Delta\Delta}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 8)$$

$$\Xi_s^*(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; -\omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{\Delta^\dagger\Delta}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 9)$$

$$\tilde{\Xi}_s^*(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; -\omega) = \lim_{\delta \rightarrow 0^+} \int \frac{d\omega'}{2\pi} \frac{S_{\Delta^\dagger\Delta^\dagger}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}'; \omega')}{\omega - \omega' + i\delta} \quad (\text{A } 10)$$

The spectral densities, in turn, are calculated by substituting the Bogoliubov-Valatin transformation (57) - (58) for the field operators $\hat{\psi}_\sigma(\mathbf{r})$ appearing in the density operators (175). Hence one is left with matrix elements involving four quasi-particle operators $\hat{\gamma}_{k\sigma}$. Employing the fermionic anticommutation relations of these operators one obtains after a lengthy but straightforward calculation

$$S_{n,n}(\mathbf{r}, \mathbf{x}, \omega) =$$

$$\begin{aligned}
& \left[\delta(\omega - (E_k + E_q)) \left(u_k^*(\mathbf{r})v_q^*(\mathbf{r}) + u_q^*(\mathbf{r})v_k^*(\mathbf{r}) \right) \right. \\
& \quad \times \left(u_k(\mathbf{x})v_q(\mathbf{x}) + u_q(\mathbf{x})v_k(\mathbf{x}) \right) \\
& - \delta(\omega + (E_k + E_q)) \left(u_k(\mathbf{r})v_q(\mathbf{r}) + u_q(\mathbf{r})v_k(\mathbf{r}) \right) \\
& \quad \times \left(u_k^*(\mathbf{x})v_q^*(\mathbf{x}) + u_q^*(\mathbf{x})v_k^*(\mathbf{x}) \right) \left. \right] \\
& + \left(f(E_k) - f(E_q) \right) \times \\
& \quad \left[\delta(\omega - (E_k - E_q)) \left(v_k^*(\mathbf{r})v_q(\mathbf{r}) - u_k^*(\mathbf{r})u_q(\mathbf{r}) \right) \right. \\
& \quad \times \left(v_q^*(\mathbf{x})v_k(\mathbf{x}) - u_q^*(\mathbf{x})u_k(\mathbf{x}) \right) \\
& - \delta(\omega + (E_k - E_q)) \left(v_k^*(\mathbf{r})v_q(\mathbf{r}) - u_k^*(\mathbf{r})u_q(\mathbf{r}) \right) \\
& \quad \times \left. \left(v_q^*(\mathbf{x})v_k(\mathbf{x}) - u_q^*(\mathbf{x})u_k(\mathbf{x}) \right) \right] \left. \right\} \tag{A 11}
\end{aligned}$$

$$\begin{aligned}
S_{n,\Delta}(\mathbf{r}, \mathbf{x}, \mathbf{x}', \omega) = & \\
& \sum_{k,q} \left\{ \left(f(E_k) + f(E_q) - 1 \right) \times \right. \\
& \quad \left[\delta(\omega - (E_k + E_q)) \left(u_k^*(\mathbf{r})v_q^*(\mathbf{r}) + u_q^*(\mathbf{r})v_k^*(\mathbf{r}) \right) u_k(\mathbf{x}')u_q(\mathbf{x}) \right. \\
& \quad \left. - \delta(\omega + (E_k + E_q)) \left(u_k(\mathbf{r})v_q(\mathbf{r}) + u_q(\mathbf{r})v_k(\mathbf{r}) \right) v_k^*(\mathbf{x}')v_q^*(\mathbf{x}) \right] \\
& + \left(f(E_k) - f(E_q) \right) \times \\
& \quad \left[\delta(\omega - (E_k - E_q)) \left(v_k^*(\mathbf{r})v_q(\mathbf{r}) - u_k^*(\mathbf{r})u_q(\mathbf{r}) \right) v_q^*(\mathbf{x})u_k(\mathbf{x}') \right. \\
& \quad \left. - \delta(\omega + (E_k - E_q)) \left(v_k^*(\mathbf{r})v_q(\mathbf{r}) - u_k^*(\mathbf{r})u_q(\mathbf{r}) \right) v_q^*(\mathbf{x}')u_k(\mathbf{x}) \right] \left. \right\} \tag{A 12}
\end{aligned}$$

$$\begin{aligned}
S_{n,\Delta^\dagger}(\mathbf{r}, \mathbf{x}, \mathbf{x}', \omega) = & \\
\sum_{k,q} \left\{ \left(f(E_k) + f(E_q) - 1 \right) \times \right. & \\
\left[\delta(\omega - (E_k + E_q)) \left(u_k^*(\mathbf{r})v_q^*(\mathbf{r}) + u_q^*(\mathbf{r})v_k^*(\mathbf{r}) \right) v_k(\mathbf{x})v_q(\mathbf{x}') \right. & \\
- \delta(\omega + (E_k + E_q)) \left(u_k(\mathbf{r})v_q(\mathbf{r}) + u_q(\mathbf{r})v_k(\mathbf{r}) \right) u_k^*(\mathbf{x})u_q^*(\mathbf{x}') & \\
+ \left(f(E_k) - f(E_q) \right) \times & \\
\left[\delta(\omega + (E_k - E_q)) \left(v_k^*(\mathbf{r})v_q(\mathbf{r}) - u_k^*(\mathbf{r})u_q(\mathbf{r}) \right) u_q^*(\mathbf{x})v_k(\mathbf{x}') \right. & \\
+ \delta(\omega - (E_k - E_q)) \left(v_k^*(\mathbf{r})v_q(\mathbf{r}) - u_k^*(\mathbf{r})u_q(\mathbf{r}) \right) u_q^*(\mathbf{x}')v_k(\mathbf{x}) \left. \right] \left. \right\} & \quad (\text{A } 13)
\end{aligned}$$

$$\begin{aligned}
S_{\Delta,n}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \omega) = & \\
\sum_{k,q} \left\{ \left(f(E_k) + f(E_q) - 1 \right) \times \right. & \\
\left[\delta(\omega - (E_k + E_q)) v_k^*(\mathbf{r})v_q^*(\mathbf{r}') \left(u_k(\mathbf{x})v_q(\mathbf{x}) + u_q(\mathbf{x})v_k(\mathbf{x}) \right) \right. & \\
- \delta(\omega + (E_k + E_q)) u_k(\mathbf{r})u_q(\mathbf{r}') \left(u_k^*(\mathbf{x})v_q^*(\mathbf{x}) + u_q^*(\mathbf{x})v_k^*(\mathbf{x}) \right) \left. \right] & \\
+ \left(f(E_k) - f(E_q) \right) \times & \\
\left[\delta(\omega + (E_k - E_q)) v_k^*(\mathbf{r}')u_q(\mathbf{r}) \left(v_q^*(\mathbf{x})v_k(\mathbf{x}) - u_q^*(\mathbf{x})u_k(\mathbf{x}) \right) \right. & \\
- \delta(\omega - (E_k - E_q)) v_k^*(\mathbf{r})u_q(\mathbf{r}') \left(v_q^*(\mathbf{x})v_k(\mathbf{x}) - u_q^*(\mathbf{x})u_k(\mathbf{x}) \right) \left. \right] \left. \right\} & \quad (\text{A } 14)
\end{aligned}$$

$$\begin{aligned}
S_{\Delta^\dagger,n}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \omega) = & \\
\sum_{k,q} \left\{ \left(f(E_k) + f(E_q) - 1 \right) \right. & \\
\left[\delta(\omega - (E_k + E_q)) u_k^*(\mathbf{r}')u_q^*(\mathbf{r}) \left(u_k(\mathbf{x})v_q(\mathbf{x}) + u_q(\mathbf{x})v_k(\mathbf{x}) \right) \right. & \\
- \delta(\omega + (E_k + E_q)) v_k(\mathbf{r}')v_q(\mathbf{r}) \left(u_k^*(\mathbf{x})v_q^*(\mathbf{x}) + u_q^*(\mathbf{x})v_k^*(\mathbf{x}) \right) \left. \right] & \\
- \left(f(E_k) - f(E_q) \right) \times & \\
\left[\delta(\omega - (E_k - E_q)) u_k^*(\mathbf{r}')v_q(\mathbf{r}) \left(v_q^*(\mathbf{x})v_k(\mathbf{x}) - u_q^*(\mathbf{x})u_k(\mathbf{x}) \right) \right. & \\
- \delta(\omega + (E_k - E_q)) u_k^*(\mathbf{r})v_q(\mathbf{r}') \left(v_q^*(\mathbf{x})v_k(\mathbf{x}) - u_q^*(\mathbf{x})u_k(\mathbf{x}) \right) \left. \right] \left. \right\} & \quad (\text{A } 15)
\end{aligned}$$

$$\begin{aligned}
S_{\Delta,\Delta}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}', \omega) = & \\
\sum_{k,q} \left\{ \left(f(E_k) + f(E_q) - 1 \right) \times \right. & \\
\left[\delta(\omega - (E_k + E_q)) v_k^*(\mathbf{r})v_q^*(\mathbf{r}')u_k(\mathbf{x}')u_q(\mathbf{x}) \right. & \\
- \delta(\omega + (E_k + E_q)) v_k^*(\mathbf{x}')v_q^*(\mathbf{x})u_k(\mathbf{r})u_q(\mathbf{r}') \left. \right] &
\end{aligned}$$

$$\left. \begin{aligned} & \left[\delta\left(\omega + (E_k - E_q)\right) v_k^*(\mathbf{r}') v_q^*(\mathbf{x}') u_k(\mathbf{x}) u_q(\mathbf{r}) \right. \\ & \left. - \delta\left(\omega - (E_k - E_q)\right) v_k^*(\mathbf{r}) v_q^*(\mathbf{x}) u_k(\mathbf{x}') u_q(\mathbf{r}') \right] \end{aligned} \right\} \quad (\text{A } 16)$$

$$\begin{aligned} S_{\Delta^\dagger, \Delta^\dagger}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}', \omega) = & \\ \sum_{k,q} \left\{ \left(f(E_k) + f(E_q) - 1 \right) \times \right. & \\ & \left[\delta\left(\omega - (E_k + E_q)\right) u_k^*(\mathbf{r}') u_q^*(\mathbf{r}) v_k(\mathbf{x}) v_q(\mathbf{x}') \right. \\ & \left. - \delta\left(\omega + (E_k + E_q)\right) u_k^*(\mathbf{x}) u_q^*(\mathbf{x}') v_k(\mathbf{r}') v_q(\mathbf{r}) \right] \\ + \left(f(E_k) - f(E_q) \right) \times & \\ & \left[\delta\left(\omega + (E_k - E_q)\right) u_k^*(\mathbf{r}) u_q^*(\mathbf{x}) v_k(\mathbf{x}') v_q(\mathbf{r}') \right. \\ & \left. - \delta\left(\omega - (E_k - E_q)\right) u_k^*(\mathbf{r}') u_q^*(\mathbf{x}') v_k(\mathbf{x}) v_q(\mathbf{r}) \right] \left. \right\} \quad (\text{A } 17) \end{aligned}$$

$$\begin{aligned} S_{\Delta, \Delta^\dagger}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}', \omega) = & \\ \sum_{k,q} \left\{ \left(f(E_k) + f(E_q) - 1 \right) \times \right. & \\ & \left[\delta\left(\omega - (E_k + E_q)\right) v_k(\mathbf{x}) v_k^*(\mathbf{r}) v_q(\mathbf{x}') v_q^*(\mathbf{r}') \right. \\ & \left. - \delta\left(\omega + (E_k + E_q)\right) u_k(\mathbf{r}) u_k^*(\mathbf{x}) u_q(\mathbf{r}') u_q^*(\mathbf{x}') \right] \\ + \left(f(E_k) - f(E_q) \right) \times & \\ & \left[\delta\left(\omega + (E_k - E_q)\right) u_q(\mathbf{r}) u_q^*(\mathbf{x}) v_k(\mathbf{x}') v_k^*(\mathbf{r}') \right. \\ & \left. - \delta\left(\omega - (E_k - E_q)\right) u_q(\mathbf{r}') u_q^*(\mathbf{x}') v_k(\mathbf{x}) v_k^*(\mathbf{r}) \right] \left. \right\} \quad (\text{A } 18) \end{aligned}$$

$$\begin{aligned} S_{\Delta^\dagger, \Delta}(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}', \omega) = & \\ \sum_{k,q} \left\{ \left(f(E_k) + f(E_q) - 1 \right) \times \right. & \\ & \left[\delta\left(\omega - (E_k + E_q)\right) u_k(\mathbf{x}') u_k^*(\mathbf{r}') u_q(\mathbf{x}) u_q^*(\mathbf{r}) \right. \\ & \left. - \delta\left(\omega + (E_k + E_q)\right) v_k(\mathbf{r}') v_k^*(\mathbf{x}') v_q(\mathbf{r}) v_q^*(\mathbf{x}) \right] \\ + \left(f(E_k) - f(E_q) \right) \times & \\ & \left[\delta\left(\omega + (E_k - E_q)\right) u_k(\mathbf{x}) u_k^*(\mathbf{r}) v_q(\mathbf{r}') v_q^*(\mathbf{x}') \right. \\ & \left. - \delta\left(\omega - (E_k - E_q)\right) u_k(\mathbf{x}') u_k^*(\mathbf{r}') v_q(\mathbf{r}) v_q^*(\mathbf{x}) \right] \left. \right\} \quad (\text{A } 19) \end{aligned}$$

These formulas were generated with MATHEMATICA [21].

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