

# DENSITY FUNCTIONAL THEORY OF NORMAL AND SUPERCONDUCTING ELECTRON LIQUIDS: EXPLICIT FUNCTIONALS VIA THE GRADIENT EXPANSION

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## Abstract

The basic idea of density functional theory is to map an interacting many-particle system on an effective non-interacting system in such a way that the ground-state densities of the two systems are identical. The non-interacting particles move in an effective local potential which is a functional of the density. The central task of density functional theory is to find good approximations for the density-dependence of this local single-particle potential. An overview of recent advances in the construction of this potential (beyond the local-density approximation) will be given along with successful applications in quantum chemistry and solid state theory. We then turn to the extension of density functional theory to superconductors and first discuss the Hohenberg-Kohn-Sham-type existence theorems. In the superconducting analogue of the the normal-state Kohn-Sham formalism, a local single-particle potential is needed which now depends on two densities, the ordinary density  $n(\mathbf{r})$  and the anomalous density  $\Delta(\mathbf{r}, \mathbf{r}')$ . As a first step towards the construction of such a potential, a gradient expansion technique for superconductors is presented and applied to calculate an approximation of the non-interacting kinetic energy functional  $T_s[n, \Delta]$ . We also obtain a Thomas-Fermi-type variational equation for superconductors.

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# 1 Introduction

The basic idea of normal-state density functional theory is to describe a many-electron system exclusively and completely in terms of its ground-state density. This means that

1. every observable quantity of a stationary quantum mechanical system can be calculated, in principle exactly, from the ground-state density alone, i. e., every observable quantity can be written as a functional of the ground-state density.
2. The ground-state density can be calculated, in principle exactly, from a variational principle involving only the density.

In the following section we shall indicate a proof of these two important statements first given by Hohenberg and Kohn (1964). We then demonstrate that the variational principle, i. e., the second of the above statements, can be cast into the form of a one-particle Schrödinger equation with a local, density-dependent single-particle potential. The resulting self-consistent scheme, known as the Kohn-Sham scheme (Kohn and Sham 1965), is the heart of modern density functional theory. In section 3 we illustrate a number of prominent methods of constructing approximations to the Kohn-Sham exchange-correlation potential along with a few applications. For a comprehensive up-to-date survey of applications of the density functional formalism the reader is referred to the proceedings of a recent NATO Advanced Study Institute (Gross and Dreizler 1994).

The original Hohenberg-Kohn-Sham formalism is a ground-state theory. Extensions have been developed for systems at finite temperature (Mermin 1965) as well as for time-dependent phenomena (Runge and Gross 1984; Gross and Kohn 1985; Wacker *et al.* 1994, Ullrich *et al.* 1995). Finite-temperature ensembles and time-dependent systems will not be pursued at length in this article. Some finite-temperature calculations are described in the review article by Kohn and Vashishta (1983). A survey of applications of time-dependent density functional theory can be found in the review article by Gross and Kohn (1990) and in the book by Mahan and Subbaswamy (1990).

The traditional density functional formalism is tailored for the description of *inhomogeneous* systems. For homogeneous media, although formally exact, density functional theory is pointless from a practical point of view in the sense that it does not help us to obtain information about the homogeneous system: The total energy per volume  $e(n)$  is trivially a function of the (constant) density  $n$ , but density functional theory gives no clue about the specific form of this function. However, the construction of many approximate exchange-correlation (xc) functionals (to be applied to inhomogeneous systems) is based on information about the xc energy and the response functions of the homogeneous gas.

Owing to a relatively large coherence length ( $10^2 - 10^4 \text{ \AA}$ ) conventional superconductivity of pure metals is well described as a phenomenon of homogeneous media. As a consequence, the development of a density functional theory for superconductors (Oliveira *et al.* 1988; Kohn *et al.* 1989; Gross and Kurth 1991) was only triggered by the advent of high-temperature superconductors. In these materials, experimental coherence lengths of the order of  $10 \text{ \AA}$  suggest that inhomogeneities on the scale of the lattice constant have to be taken into account.

In section 4 of this article we review the Hohenberg-Kohn-Sham theorems for superconductors. In addition to the ordinary density, this formalism requires a second quantity, the anomalous density  $\Delta(\mathbf{r}, \mathbf{r}')$ , whose diagonal terms  $\Delta(\mathbf{r}) \equiv \Delta(\mathbf{r}, \mathbf{r})$  reduce to the Ginzburg-Landau (Ginzburg and Landau 1950) order parameter in the appropriate limits (Gorkov 1959). The density functional formalism for superconductors leads to a set of Kohn-Sham equations whose algebraic structure is similar to the Bogoliubov-deGennes equations (de Gennes 1966). The Kohn-Sham potentials in these Bogoliubov-type equations contain, besides the usual mean-field terms, xc functionals which formally incorporate all superconducting correlations exactly. In practice, these functionals have to be approximated. For superconductors, the development of suitable approximations is still in an infant stage. A local-density approximation based on the lowest-order exchange diagram has recently been suggested (Gross and Kurth 1993; Gross *et al.* 1994). In sections 5 and 6 of this article, first steps towards a gradient expansion for superconductors are presented. Explicit results are obtained for the kinetic-energy functional. Finally, in section 7, we discuss the resulting variational equation which can be viewed as a Thomas-Fermi equation for superconductors.

For homogeneous systems,  $\Delta(\mathbf{r}, \mathbf{r}')$  is a function of  $(\mathbf{r} - \mathbf{r}')$  only, whose Fourier transform,  $\Delta(\mathbf{p})$ , is the central quantity in the traditional BCS description (Bardeen *et al.* 1957) of superconductors. A prominent feature of the density functional theory for superconductors is the appearance of a nonlocal order parameter  $\Delta(\mathbf{r}, \mathbf{r}')$ . Switching into a mixed representation in space and momentum,  $\Delta(\mathbf{R}, \mathbf{p})$  [to be precise, the Wigner transform of  $\Delta(\mathbf{r}, \mathbf{r}')$ ], the Gorkov limit of a purely space dependent order parameter  $\Delta(\mathbf{R})$  as well as the BCS limit of a purely momentum dependent gap function  $\Delta(\mathbf{p})$  are both accommodated in a natural way. The small coherence length of the high- $T_c$  superconductors suggests that a description in terms of a momentum *and* space dependent order parameter  $\Delta(\mathbf{R}, \mathbf{p})$  becomes important, where the  $\mathbf{R}$ -dependence takes inhomogeneities on the scale of the lattice constant into consideration. One can hope that the systematic treatment of spatial variations by means of the gradient expansion, as presented in this paper, will contribute to a better understanding of these materials.

## 2 Hohenberg-Kohn-Sham formalism for normal systems

We begin with a short summary of the original Hohenberg-Kohn (HK) theorem (Hohenberg and Kohn 1964).

Consider a system of  $N$  electrons characterized by the time-independent Hamiltonian

$$\hat{H}_V = \hat{T} + \hat{V} + \hat{U} \quad (1)$$

which, in second quantized notation, is given by

$$\hat{T} = \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left( -\frac{\hbar^2 \nabla^2}{2m} \right) \hat{\psi}_\sigma(\mathbf{r}) \quad (2)$$

$$\hat{V} = \sum_{\sigma=\uparrow\downarrow} \int d^3r v(\mathbf{r}) \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \quad (3)$$

$$\hat{U} = \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3r \int d^3r' \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}') \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \hat{\psi}_{\sigma'}(\mathbf{r}') \hat{\psi}_\sigma(\mathbf{r}) \quad . \quad (4)$$

For simplicity we consider only potentials  $v(\mathbf{r})$  leading to a non-degenerate ground state  $\Psi$  [extension of the HK theorem to degenerate ground states is straightforward (Kohn 1985; Dreizler and Gross 1990)]:

$$\hat{H}_V \Psi = E_{gs} \Psi \quad . \quad (5)$$

The restriction to non-degenerate ground states allows us to define a formal map

$$\mathcal{A} : v(\mathbf{r}) \longrightarrow \Psi \quad (6)$$

that maps each potential  $v(\mathbf{r})$  onto the ground-state solution  $\Psi$  of (5). For each  $\Psi$  we then calculate the ground-state density

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = \langle \Psi | \sum_{\sigma} \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) | \Psi \rangle \quad (7)$$

which establishes a second map

$$\mathcal{B} : \Psi \longrightarrow n(\mathbf{r}) \quad . \quad (8)$$

Combining  $\mathcal{A}$  and  $\mathcal{B}$  we can map each potential  $v(\mathbf{r})$  onto a density  $n(\mathbf{r})$

$$\mathcal{G} : v(\mathbf{r}) \longrightarrow n(\mathbf{r}) \quad . \quad (9)$$

The central statement of the HK theorem is that the map  $\mathcal{G}$  is invertible up to within a trivial additive constant in the potential. In order to prove this statement we have to show that the maps  $\mathcal{A}$  and  $\mathcal{B}$  are invertible.

For the map  $\mathcal{A}$ , the invertibility proof is trivial: Solving the Schrödinger equation (5) for  $V$  defines the inverse map  $\mathcal{A}^{-1}$  explicitly:

$$v(\mathbf{r}_1) + v(\mathbf{r}_2) + \dots + v(\mathbf{r}_N) + \text{const} = \frac{(\hat{T} + \hat{U})\Psi(\mathbf{r}_1 \dots \mathbf{r}_N)}{\Psi(\mathbf{r}_1 \dots \mathbf{r}_N)} = \mathcal{A}^{-1}\Psi \quad . \quad (10)$$

In the case of map  $\mathcal{B}$  one has to show that two different ground states  $\Psi \neq \Psi'$  (arising from two different potentials  $v \neq v' + \text{const}$ ) always lead to different ground-state densities  $n(\mathbf{r}) \neq n'(\mathbf{r})$ . The argument is based on the Rayleigh-Ritz principle:

$$\begin{aligned} E_{gs} &= \langle \Psi | \hat{H}_V | \Psi \rangle \\ &< \langle \Psi' | \hat{H}_V | \Psi' \rangle = \langle \Psi' | \hat{H}_{V'} + \hat{V} - \hat{V}' | \Psi' \rangle = E'_{gs} + \int d^3r n'(\mathbf{r}) (v(\mathbf{r}) - v'(\mathbf{r})) \quad . \end{aligned} \quad (11)$$

Owing to the restriction to non-degenerate ground states, (11) is a *strict* inequality. An analogous argument starting with  $E'_{gs}$  leads to

$$E'_{gs} < E_{gs} + \int d^3r n(\mathbf{r}) (v'(\mathbf{r}) - v(\mathbf{r})) \quad . \quad (12)$$

The proof is by reductio ad absurdum: assuming  $n(\mathbf{r}) = n'(\mathbf{r})$ , the addition of (11) and (12) leads to the contradiction

$$E_{gs} + E'_{gs} < E_{gs} + E'_{gs} \quad (13)$$

and one concludes that  $\mathcal{B}$  is invertible. This means that, given a non-degenerate ground-state density  $n(\mathbf{r})$ , there exists one and only one ground-state wave function  $\Psi[n]$  that reproduces that density:

$$\mathcal{B}^{-1} : n(\mathbf{r}) \longrightarrow \Psi[n] \quad . \quad (14)$$

In view of the fact that there exist infinitely many  $N$ -particle functions  $\chi(\mathbf{r}_1 \dots \mathbf{r}_N)$  which reproduce a given density  $n(\mathbf{r})$  (Harriman 1981; Zumbach and Maschke 1983), the 1–1 correspondence between *ground-state* wave functions and *ground-state* densities is a rather surprising fact.

Moreover, due to the invertibility of the two maps  $\mathcal{A}$  and  $\mathcal{B}$ , single-particle potentials  $v(\mathbf{r})$  and ground-state densities  $n(\mathbf{r})$  are in 1–1 correspondence,

$$\mathcal{G}^{-1} : n(\mathbf{r}) \longrightarrow v[n](\mathbf{r}) \quad , \quad (15)$$

i. e., given a non-degenerate ground-state density  $n(\mathbf{r})$  there exists one and only one single-particle potential  $v[n]$  that leads to this density.

Since every wave function  $\Phi$  (not only the ground-state wave function !) is trivially a functional of the external potential  $v(\mathbf{r})$

$$\Phi = \Phi[v] \quad (16)$$

and since  $v$  (by the above argument) is a functional of  $n$

$$v = v[n] \quad , \quad (17)$$

every quantum mechanical observable, i. e., every expectation value  $\langle \Phi | \hat{O} | \Phi \rangle$  is a functional of the ground-state density

$$O[n] = \langle \Phi[v[n]] | \hat{O} | \Phi[v[n]] \rangle \quad . \quad (18)$$

This proves the first statement made in the introduction.

Consider now a *specific* system whose ground-state density  $n_0(\mathbf{r})$  and ground-state energy  $E_0$  are to be calculated. The specific system is characterized by a *given* external potential  $v_0(\mathbf{r})$ . For example, for an  $\text{H}_2$  molecule,  $v_0$  is the Coulomb potential of the two protons; for a graphite crystal,  $v_0$  is the Coulomb potential of the periodic lattice of carbon nuclei. As an important second statement, the HK theorem then establishes the variational character of the energy functional

$$E_{v_0}[n] = \langle \Psi[n] | \hat{T} + \hat{U} + \hat{V}_0 | \Psi[n] \rangle \quad . \quad (19)$$

Given a density  $n(\mathbf{r})$ , the ground-state wave function  $\Psi[n]$  and thus the value of the functional  $E_{v_0}[n]$  are formally generated via the map  $\mathcal{B}^{-1}$ . By virtue of the Rayleigh-Ritz principle,  $E_{v_0}[n]$  has the property

$$\begin{aligned} E_{v_0}[n] &> E_0 && \text{for } n(\mathbf{r}) \neq n_0(\mathbf{r}) \\ E_{v_0}[n] &= E_0 && \text{for } n(\mathbf{r}) = n_0(\mathbf{r}) \quad . \end{aligned} \quad (20)$$

As a consequence, the Euler equation

$$\frac{\delta}{\delta n(\mathbf{r})} \left[ E_{v_0}[n] - \mu \int d^3r' n(\mathbf{r}') \right] = 0 \quad (21)$$

can be used to calculate the exact ground-state density  $n_0(\mathbf{r})$ . This proves the second statement made in the introduction.

Writing

$$E_{v_0}[n] = F[n] + \int d^3r n(\mathbf{r})v_0(\mathbf{r}) \quad , \quad (22)$$

one observes that the dependence of  $E_{v_0}[n]$  on the potential  $v_0(\mathbf{r})$  of the particular system considered is rather simple. The non-trivial part of the functional  $E_{v_0}[n]$ , i. e., the functional

$$F[n] = \langle \Psi[n] | \hat{T} + \hat{U} | \Psi[n] \rangle = T[n] + U[n] \quad , \quad (23)$$

is independent of  $v_0$ . In other words, the functional  $F[n]$  is *universal* in the sense that  $F[n]$  is the same functional for *all* Coulombic systems.

The three statements

- (i) 1-1 correspondence between potentials and ground-state densities
- (ii) the variational principle (21) and
- (iii) the universality of the functional  $F[n]$

comprise the HK theorem in its original form.

One problem in the original formulation of HK is the fact that the functional  $E_{v_0}[n]$  is defined (by construction) only for those functions  $n(\mathbf{r})$  that are ground-state densities of some potential (such functions  $n(\mathbf{r})$  are called  $v$ -representable). An extension of the functional  $E_{v_0}[n]$  to *arbitrary* functions  $n(\mathbf{r})$  is provided by the constrained-search formulation of Levy and Lieb (Levy 1979; Lieb 1982, 1983, 1985).

The variational principle of HK allows us to determine the ground-state density of a given many-electron system. Kohn and Sham (1965) established a scheme which yields the exact ground-state density via an intermediary orbital picture. In order to derive this scheme, let us first consider a system of *non-interacting* electrons with density  $n_s(\mathbf{r})$ , characterized by the Hamiltonian

$$\hat{H}_s = \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right) \hat{\psi}_\sigma(\mathbf{r}) \quad . \quad (24)$$

The HK theorem (applied to the case  $U \equiv 0$ ) guarantees the 1-1 correspondence between the densities  $n_s(\mathbf{r})$  and the potentials  $v_s(\mathbf{r})$ . While the functional  $F[n]$ , Eq. (23), is universal with respect to the external potential  $v_0$ , it evidently depends on the particle-particle interaction  $U$ . For the particular case  $U \equiv 0$ ,  $F[n]$  reduces to the kinetic-energy functional  $T_s[n]$  of non-interacting particles, and the total-energy functional can be written as

$$E_{v_s}^{\text{non-int}}[n] = T_s[n] + \int d^3r' n(\mathbf{r}') v_s(\mathbf{r}') \quad . \quad (25)$$

The HK variational principle (21) then reads

$$\begin{aligned} 0 &= \frac{\delta}{\delta n(\mathbf{r})} \left[ E_{v_s}^{\text{non-int}}[n] - \mu \int d^3r' n(\mathbf{r}') \right] \\ &= \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) - \mu \quad . \end{aligned} \quad (26)$$

Eq. (26) provides an exact way of calculating the ground-state density  $n_s$ . Alternatively, we can of course calculate the exact ground-state density by solving the Schrödinger equation

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad (27)$$

$$n_s(\mathbf{r}) = \sum_{\text{lowest } N} |\varphi_j(\mathbf{r})|^2 \quad . \quad (28)$$

The two ways of calculating  $n_s$ , either from (26) or from (27), (28), are completely equivalent.



Now we return to the problem of  $N$  *interacting* electrons moving in the potential  $v(\mathbf{r})$ . The HK energy functional then reads

$$E_v[n] = T[n] + U[n] + \int d^3r n(\mathbf{r})v(\mathbf{r}) \quad . \quad (29)$$

By addition and subtraction we can write

$$\begin{aligned} E_v[n] &= T_s[n] \\ &+ \int d^3r n(\mathbf{r})v(\mathbf{r}) + \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \end{aligned} \quad (30)$$

where the xc-energy functional is defined as

$$E_{xc}[n] = T[n] - T_s[n] + U[n] - \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad . \quad (31)$$

As before,  $T_s[n]$  is the kinetic-energy functional of non-interacting particles. Application of the HK variational principle (21) now yields

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \left( v(\mathbf{r}) + e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right) = \mu \quad . \quad (32)$$

Eq. (32) is formally identical with the Euler equation (26) of non-interacting particles moving in the effective single-particle potential

$$v_s(\mathbf{r}) = v(\mathbf{r}) + e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}) \quad (33)$$

with

$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad . \quad (34)$$

As emphasized above, Eq. (26) and Eqs. (27), (28) are completely equivalent methods of calculating the density. Therefore, instead of using Eq. (32), we can calculate the exact ground-state density via the single-particle Schrödinger equation

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + v_s[n](\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad (35)$$

$$n(\mathbf{r}) = \sum_{\text{lowest } N} |\varphi_j(\mathbf{r})|^2 \quad . \quad (36)$$

These are the Kohn-Sham (KS) equations. The proof shows that the KS theorem is merely a tricky way of rewriting the HK variational principle.

Having found a self-consistent solution of the KS equations, the kinetic energy  $T_s[n]$  can be calculated from

$$\begin{aligned} T_s[n] &= \sum_j \int d^3r \varphi_j^*(\mathbf{r}) \left( -\frac{\hbar^2 \nabla^2}{2m} \right) \varphi_j(\mathbf{r}) \\ &= \sum_j \int d^3r \varphi_j^*(\mathbf{r}) (\varepsilon_j - v_s[n](\mathbf{r})) \varphi_j(\mathbf{r}) \\ &= \sum_j \varepsilon_j - \int d^3r n(\mathbf{r})v_s[n](\mathbf{r}) \quad . \end{aligned} \quad (37)$$

Insertion in Eq. (30) leads to the following exact representation of the ground-state energy:

$$\begin{aligned}
E_{gs} &= \sum_{j=1}^N \varepsilon_j - \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
&\quad - \int d^3r n(\mathbf{r})v_{xc}[n](\mathbf{r}) + E_{xc}[n] \quad .
\end{aligned}
\tag{38}$$

By virtue of Eq. (37) the non-interacting kinetic energy functional  $T_s[n]$  is treated *exactly* within the KS scheme; only the xc part  $E_{xc}[n]$  of the total functional

$$F[n] = T_s[n] + E_{xc}[n] + \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
\tag{39}$$

needs to be approximated. Direct use of the HK variational principle (21), on the other hand, requires approximations of  $T_s[n]$  as well. The Thomas-Fermi model and its extensions fall in this category [for a review see chapter 5 of Dreizler and Gross (1990)]. The approximations of  $T_s[n]$  employed in these models seriously reduce the accuracy of the results. It is therefore preferable to use the KS scheme for practical calculations although, on the exact level, the HK variational principle and the KS scheme are rigorously equivalent.

One has to emphasize that the ground-state Slater determinant constructed from the KS orbitals  $\varphi_j$  must not be interpreted as an approximation of the true many-particle ground state. Only the densities calculated via the KS scheme and the total energies obtained from (38) are identical with the exact ground-state densities and energies.

We finally mention that the traditional HK and KS theorems are easily extended to a wide variety of cases of physical interest including spin-polarized systems (von Barth and Hedin 1972; Rajagopal and Callaway 1973), orbital currents (Vignale and Rasolt 1987, 1988), multi-component systems (Sander *et al.* 1973; Kalia and Vashishta 1978), thermal ensembles (Mermin 1965) and relativistic systems (Rajagopal and Callaway 1973; Rajagopal 1978; MacDonald and Vosko 1979; Ramana and Rajagopal 1983).

Until now we have proved some rigorous but rather formal existence theorems. It might appear that density functional theory is a rather esoteric theory with few applications. This is by no means the case; in solid-state physics, at least 95 % of all band structure calculations are done with the KS scheme described above. In order to actually apply the KS formalism to real systems one has to find adequate approximations of the xc-energy functional.

### 3 Approximate exchange-correlation functionals in normal-state density functional theory

#### 3.1 The local density approximation

The most widely used and for many purposes surprisingly accurate approximation of the xc energy functional is the local density approximation (LDA)

$$E_{xc}^{LDA}[n] = \int d^3r e_{xc}^{hom}(n(\mathbf{r})) \quad (40)$$

which leads to

$$v_{xc}^{LDA}[n](\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[n]}{\delta n(\mathbf{r})} = \left. \frac{de_{xc}^{hom}(n)}{dn} \right|_{n=n(\mathbf{r})} . \quad (41)$$

$e_{xc}^{hom}(n)$  is the xc energy per unit volume of the *homogeneous* electron gas which is well known from Quantum Monte Carlo calculations and from many-body perturbation theory. The analogous approximation for spin-polarized systems is the local spin density approximation (LSD)

$$E_{xc}^{LSD}[n_{\uparrow}, n_{\downarrow}] = \int d^3r e_{xc}^{hom}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) \quad (42)$$

where

$$n_{\sigma}(\mathbf{r}) = \sum_{\text{occupied}} |\varphi_{i\sigma}(\mathbf{r})|^2 , \quad \sigma = \uparrow\downarrow . \quad (43)$$

In practical calculations one uses parametrizations for  $e_{xc}^{hom}$ . Currently the best parametrizations available are the ones by Vosko, Wilk and Nusair (1980) and by Perdew and Zunger (1981).

By its very construction, one might expect the LDA to give good results only for weakly inhomogeneous systems, i. e., for systems whose density varies very slowly in space. However, contrary to this expectation, the LDA performs quite well even for strongly inhomogeneous systems such as atoms, molecules and solids. Total atomic and molecular ground-state energies typically lie within 1.5 % of the experimental value. Molecular equilibrium distances are usually reproduced within 3 % of the experimental data. The Fermi surface of metals is reproduced within a few percent, even for strongly correlated systems such as the heavy-fermion metals. Lattice constants are typically within 3 % of experimental data.

Other quantities such as the band gaps of insulators and semiconductors are not well reproduced. LDA band gaps are often 40 % off the experimental value. The reason for this failure is a complicated one: While, on one hand, the band gap is an excitation energy (and therefore beyond the realm of ordinary ground-state density functional theory), it

may on the other hand be expressed as the difference between the ionization potential  $I$  and the electron affinity  $A$ :

$$E_{gap} = I - A = E_{gs}(N + 1) - 2E_{gs}(N) + E_{gs}(N - 1) \quad . \quad (44)$$

Here,  $E_{gs}(N)$  is the ground-state energy of the insulating  $N$ -particle system, and  $E_{gs}(N \pm 1)$  is the ground-state energy of the same system [i. e., the same  $v_0(\mathbf{r})$ ] with one electron more or less, respectively. Thus the band gap can be represented in terms of ground-state energies corresponding to systems with different particle numbers. A careful analysis shows (Perdew *et al.* 1982; Perdew and Levy 1983; Sham and Schlüter 1983; Perdew 1985; Sham 1985; Sham and Schlüter 1985; Hanke *et al.* 1985; Kohn 1986; Perdew 1986a) that the exact xc potential  $v_{xc}^{exact}[n](\mathbf{r})$  has discontinuities as a function of the particle number  $N$ . In the calculation of the band gap from (44), these discontinuities need to be taken into account. One obtains the exact formula [see, e. g., Dreizler and Gross (1990), chapter 6.3]

$$E_{gap} = \varepsilon_C - \varepsilon_V + \lim_{\delta \rightarrow 0^+} \left( v_{xc} \Big|_{N+\delta} - v_{xc} \Big|_{N-\delta} \right) \quad (45)$$

where  $\varepsilon_V$  is the highest KS orbital energy of the valence band while  $\varepsilon_C$  is the lowest KS energy of the conduction band. Since  $v_{xc}^{LDA}$  is a continuous function of  $N$ , the last term of (45) vanishes within the LDA and the gap is poorly reproduced.

Besides that, strongly correlated systems such as  $\text{La}_2\text{CuO}_4$  and the transition metal oxides are predicted to be metals in LDA while, in reality, these materials are antiferromagnetic insulators or semiconductors. One might be tempted to conclude that, by its very nature, the KS scheme, being a mean-field-type approximation, cannot describe strongly correlated systems. At this point one has to emphasize that the KS scheme is *not* a mean-field approximation. As a matter of principle, the KS scheme is exact. The fact that strongly correlated systems are not properly accounted for is entirely due to the crudeness of the LDA. An adequate description of strongly correlated systems calls for better functionals.

The LDA is deficient mainly in two respects: (i) Nonlocalities are completely neglected in the LDA, i. e., the xc potential at point  $\mathbf{r}$  is entirely determined by the density at the very same point  $\mathbf{r}$ . The systematic incorporation of nonlocal effects is possible via the so-called density-gradient expansion which will be discussed in section 3.2. (ii) The LDA total-energy functional contains a self-interaction error arising from the fact that the self-Coulomb energy contained in

$$E_H[n] = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (46)$$

is not cancelled exactly by  $E_{xc}^{LDA}$ . As a consequence,  $v_{xc}^{LDA}(\mathbf{r})$  falls off exponentially for large  $r$  while  $v_{xc}^{exact}$  falls off as  $-\frac{e^2}{r}$  for neutral atoms and molecules. Self-interaction

corrected (SIC) functionals will be discussed in sections 3.3 and 3.4. It will turn out that even strongly correlated systems can be described quite well with SIC functionals.

### 3.2 Density-gradient expansion and generalized gradient approximation

A way of systematically including inhomogeneity corrections to the LDA is the density-gradient expansion. The latter can be constructed for the functionals  $T_s[n]$ ,  $E_x[n]$  and  $E_c[n]$ .

The common starting point for the gradient expansions of  $T_s[n]$  and  $E_x[n]$  is the one-particle density matrix

$$\gamma_s(\mathbf{r}, \mathbf{r}') = \sum_{j: \epsilon_j \leq \epsilon_F} \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \quad , \quad (47)$$

calculated from the solutions of the single-particle Schrödinger equation

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r}) \quad . \quad (48)$$

For simplicity we consider only the case of even particle number and vanishing spin polarization, so that each orbital below the Fermi level in (47) appears twice, once for spin-up and once for spin-down. With the help of the so-defined density matrix which, according to the HK theorem, is a unique functional of the ground state density  $n(\mathbf{r})$ , the kinetic and exchange energy functionals are readily expressed:

$$T_s[n] = \frac{\hbar^2}{2m} \int d^3r [\nabla_r \cdot \nabla_{r'} \gamma_s(\mathbf{r}, \mathbf{r}')]_{\mathbf{r}=\mathbf{r}'} \quad (49)$$

$$E_x[n] = -\frac{e^2}{4} \int d^3r \int d^3r' \frac{|\gamma_s(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad . \quad (50)$$

Thus, any approximation of the density matrix  $\gamma_s[n]$  leads directly to approximate functionals for  $T_s[n]$  and  $E_x[n]$ .

The construction of the gradient expansion then basically consists of three steps:

1. Starting point is a semiclassical expansion (i. e., an expansion in powers of  $\hbar$ ) of the density matrix (47). This leads to an expression for the density matrix in terms of the local chemical potential

$$\mu(\mathbf{r}) = \mu - v_s(\mathbf{r}) \quad (51)$$

and its derivatives:

$$\gamma_s = \gamma_s(\mu, \partial_i \mu, \partial_j \partial_k \mu, \dots) \quad . \quad (52)$$

For normal-state systems, Eq. (52) only contains even powers of  $\hbar$  (Grammaticos and Voros 1979). Such a semiclassical expansion has first been systematically performed by Kirzhnits (1957, 1967); his technique, however, cannot readily be applied to the superconducting case. In section 5 we shall therefore choose a slightly different

approach to the problem that goes back to the work of Baraff and Borowitz (1961) and start with a semiclassical expansion of the one-particle Green's function for a non-interacting system; from there we calculate the density matrix.

2. In the next step, one determines  $n(\mathbf{r})$  from the diagonal of the density matrix (52). The functional  $n[\mu]$  is then inverted consistently up to the same maximum order in  $\hbar$ . This yields an approximation of the functional  $\mu[n](\mathbf{r})$ :

$$\mu = \mu\left(n, \partial_i n, \partial_j \partial_k n, \dots\right) \quad . \quad (53)$$

3. Finally, this expression is inserted in Eq. (52). In this fashion, one obtains approximations of the density functional  $\gamma_s[n]$  and hence, by (49) and (50), also for the functionals  $T_s[n]$  and  $E_x[n]$ .

One ends up with the following results:

$$\begin{aligned} T_s[n] &= T_s^{(0)}[n] + T_s^{(2)}[n] + \dots \\ &= \frac{3\hbar^2(3\pi^2)^{\frac{2}{3}}}{10m} \int d^3r n^{\frac{5}{3}} + \frac{\hbar^2}{72m} \int d^3r \frac{(\nabla n)^2}{n} + \dots \end{aligned} \quad (54)$$

$$\begin{aligned} E_x[n] &= E_x^{(0)}[n] + E_x^{(2)}[n] + \dots \\ &= -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} e^2 \int d^3r n^{\frac{4}{3}} - \frac{7e^2}{432\pi(3\pi^2)^{\frac{1}{3}}} \int d^3r \frac{(\nabla n)^2}{n^{\frac{4}{3}}} - \dots \end{aligned} \quad (55)$$

$T_s^{(0)}$  and  $E_x^{(0)}$  are identical with the functionals first introduced by Thomas (1927) and Fermi (1928) and by Dirac (1930), and  $T_s^{(2)}$  has the same functional form as the traditional von Weizsäcker functional (von Weizsäcker 1935). The calculation of  $E_x^{(2)}[n]$  involves the introduction of convergence factors (Sham 1971; Gross and Dreizler 1981) which is somewhat problematic. Recent recalculations of the second-order exchange energy functional by Kleinman and collaborators (Kleinman 1984; Antoniewicz and Kleinman 1985; Kleinman and Lee 1988), Chevary and Vosko (1988) and Engel and Vosko (1990) have shown that  $E_x^{(2)}[n]$  should be corrected by a factor of  $\frac{10}{7}$ .

The calculation of the first gradient term of the correlation energy functional has turned out to be an extremely difficult task. Many authors contributed to its calculation (Ma and Brueckner 1968; Rasolt and Geldart 1975, 1986; Geldart and Rasolt 1976, 1987; Langreth and Perdew 1975, 1977, 1979, 1980, 1982; Langreth and Mehl 1981, 1983; Hu and Langreth 1985, 1986) employing methods which are usually different from the semiclassical expansion described above. The analytic structure of this term is as follows:

$$E_c^{(2)}[n] = \int d^3r f(n(\mathbf{r})) \frac{(\nabla n(\mathbf{r}))^2}{n(\mathbf{r})^{4/3}} \quad . \quad (56)$$

The *function*  $f(n)$  is fairly well known for densities in the range  $0 \leq r_s \leq 6$ , where  $r_s$  is the Wigner-Seitz radius. For a comparison of different results for  $f(n)$ , the reader is referred to Dreizler and Gross (1990), chapter 7.6.

The currently best functionals involving density gradients are the so-called generalized gradient approximations (GGA) (Langreth and Mehl 1981, 1983; Hu and Langreth 1985, 1986; Becke 1986, 1988; Perdew and Wang 1986, 1992; Perdew 1986b, 1991; DePristo and Kress 1987; Vosko and MacDonald 1987; Lee *et al.* 1988; Wilson and Levy 1990; Engel *et al.* 1992; Engel and Vosko 1993a, 1993b) which can be viewed as heuristic resummations of the gradient expansion.

As examples we give here the exchange energy functional of Becke (1988)

$$e_x = -A_x n^{4/3} \left[ 1 - \frac{\beta}{2^{1/3} A_x} \frac{x^2}{1 + 6\beta x \sinh^{-1}(x)} \right] \quad (57)$$

where  $x = 2^{1/3} |\nabla n| / n^{4/3}$ ,  $A_x = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3}$  and  $\beta = 0.0042$ , and the correlation energy functional of Lee, Yang, and Parr (1988)

$$e_c = -\frac{a}{1 + d n^{-1/3}} \left\{ n + b n^{-2/3} \left[ C_F n^{5/3} - 2 t_W + \frac{1}{9} \left( t_W + \frac{\nabla^2 n}{2} \right) \right] \exp \left( -c n^{-1/3} \right) \right\} \quad (58)$$

where

$$t_W = \frac{1}{8} \left( \frac{|\nabla n|^2}{n} - \nabla^2 n \right) \quad , \quad (59)$$

and  $C_F = 3/10(3\pi^2)^{2/3}$ ,  $a = 0.049$ ,  $b = 0.132$ ,  $c = 0.2533$ , and  $d = 0.349$ .

Table 1 shows total atomic ground-state energies of the first-row atoms. The results of self-consistent KS calculations with the Becke-Lee-Yang-Parr (BLYP) functional resulting from adding Eqs. (57) and (58), and the GGA by Perdew and Wang (PW91) (Perdew 1991; Perdew and Wang 1992) are given together with LDA results (Perdew and Zunger 1981; Norman and Koelling 1984). Comparison with the exact values of Davidson *et al.* (1991) given in the last column of Table 1 shows that the GGAs lead to a considerable improvement over the LDA. For the LDA the mean absolute deviation  $\bar{\Delta}$  is 384 mH while for the two GGAs one finds 10.8mH and 11.4mH, respectively.

In a recent study of all 32 neutral molecules that can be formed from H and the first-row atoms, Pople and coworkers (Gill *et al.* 1992; Pople *et al.* 1992; Johnson *et al.* 1992, 1993) found that the KS scheme combined with GGAs for the xc energy functional outperformed some of the traditional methods of quantum chemistry: For the above molecules, the mean absolute deviation of the atomization energies from experimental values was 5.6 kcal/mol for the BLYP functional as compared to 85.9 kcal/mol for Hartree-Fock and 22.4 kcal/mol for second-order Møller-Plesset theory.

In all systems investigated so far, the GGAs performed at least as well as the LSD (Engel *et al.* 1992; Zhu *et al.* 1992; Miehlich *et al.* 1989; Juan and Kaxiras 1993) and in most systems much better than the LDA.

We finally mention that the GGA potential of Engel and Vosko (1993b) was found to correctly predict FeO and CoO as antiferromagnetic insulators (Dufek *et al.* 1994).

### 3.3 SIC functionals

In spite of their impressive accuracy for ground-state energies, the GGAs are still deficient regarding the self-interaction error. As in LDA, the correct  $-\frac{e^2}{r}$  tail of  $v_{xc}^{exact}$  is not reproduced by the GGAs. As a consequence, negative ions are usually not bound so that electron affinities cannot be calculated. Various approaches to self-interaction corrected (SIC) functionals have been proposed (Perdew 1979; Perdew and Zunger 1981; Dobson and Rose 1982; Dobson 1991, 1992, 1993). So far, most calculations have been performed with the SIC functional of Perdew and Zunger (1981) which is constructed as follows: Given an approximate (not self-interaction corrected) xc energy functional  $E_{xc}^{approx}$ , a self-interaction corrected functional is defined by

$$\begin{aligned} E_{xc}^{SIC}[n_{\uparrow}, n_{\downarrow}] &= E_{xc}^{approx}[n_{\uparrow}, n_{\downarrow}] \\ &- \sum_i (E_H[n_{i\uparrow}] + E_{xc}^{approx}[n_{i\uparrow}, 0]) \\ &- \sum_i (E_H[n_{i\downarrow}] + E_{xc}^{approx}[0, n_{i\downarrow}]) \end{aligned} \quad (60)$$

with  $E_H[n]$  given by Eq. (46) and

$$n_{i\sigma}(\mathbf{r}) = |\varphi_{i\sigma}(\mathbf{r})|^2 \quad . \quad (61)$$

This functional predicts electron affinities rather successfully (Cole and Perdew 1982) if  $E_{xc}^{approx} = E_{xc}^{LSD}$ . A difficulty of  $E_{xc}^{SIC}$  arising for solids is that the self-interaction correction vanishes if Bloch states are used in Eq. (61). This problem can be circumvented if the self-interaction correction to the total energy is expressed in terms of Wannier functions. Periodic SIC potentials for the Bloch states are then derived variationally from the energy functional (Harrison *et al.* 1983; Heaton *et al.* 1983).

Another drawback of the above SIC functional is the fact that the single-particle potential appearing in the SIC-KS equations is a different one for each orbital. Projection techniques have been proposed (Heaton *et al.* 1983; Szotek *et al.* 1994) to remove this formal ugliness.

SIC functionals have proven to be very successful, even in the description of strongly correlated systems: MnO, FeO, CoO, NiO, and CuO are correctly predicted to be antiferromagnetic insulators while VO is properly predicted to be a nonmagnetic metal (Szotek



*et al.* 1993; Svane and Gunnarson 1990), The calculated band gaps and magnetic moments are in good agreement with experiment. Apart from the transition metal oxides,  $\text{La}_2\text{CuO}_4$  is correctly predicted to have an antiferromagnetic semiconducting state. The band gap of 2.1 eV and spin magnetic moment of  $0.66 \mu_B$  compare favourably with experiment (Temmerman *et al.* 1993). Most recently, the SIC functionals were also found to give a successful description of the  $\gamma \rightarrow \alpha$  transition in Ce (Szotek *et al.* 1994; Svane 1994).

### 3.4 Optimized potential method

The conventional density functional approach to the calculation of many-electron ground state properties involves approximations of the xc energy  $E_{xc}[n]$  as explicit functionals of the density  $n$ . The xc potential is then defined as functional derivative of  $E_{xc}$ , see Eq. (34). However, there exists an alternative approach within the framework of density functional theory, the so-called optimized potential method (OPM) first suggested by Sharp and Horton (1953) and later refined by Talman and Shadwick (1976). In contrast to Eq. (30), the total energy

$$E^{\text{OPM}}[\varphi_1 \dots \varphi_N] = \sum_{j=1}^N \int d^3r \varphi_j^*(\mathbf{r}) \left( -\frac{\hbar^2 \nabla^2}{2m} \right) \varphi_j(\mathbf{r}) + \int d^3r n(\mathbf{r}) v(\mathbf{r}) + \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[\varphi_1 \dots \varphi_N] \quad (62)$$

is now written as a functional of  $N$  single-particle orbitals  $\{\varphi_j(\mathbf{r})\}$  resulting from a Schrödinger equation with a local effective potential:

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad . \quad (63)$$

The optimized effective potential,  $v^{\text{OPM}}(\mathbf{r})$ , is determined by requiring the orbitals to be the ones that minimize the energy functional (62). The stationarity condition

$$\left. \frac{\delta E^{\text{OPM}}}{\delta v_s(\mathbf{r})} \right|_{v_s=v^{\text{OPM}}} = 0 \quad (64)$$

leads to the following integral equation for an optimized xc potential:

$$\sum_{j=1}^N \int d^3r' \left[ v_{xc}^{\text{OPM}}(\mathbf{r}') \varphi_j^*(\mathbf{r}') - \frac{\delta E_{xc}[\varphi_1 \dots \varphi_N]}{\delta \varphi_j(\mathbf{r}')} \right] \varphi_j(\mathbf{r}) \sum_{\substack{k=1 \\ k \neq j}}^{\infty} \frac{\varphi_k^*(\mathbf{r}) \varphi_k(\mathbf{r}')}{\varepsilon_j - \varepsilon_k} + c.c. = 0 \quad (65)$$

where

$$v_{xc}^{\text{OPM}}(\mathbf{r}) \equiv v^{\text{OPM}}(\mathbf{r}) - v(\mathbf{r}) - e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad . \quad (66)$$

We emphasize that from a fundamental point of view the total-energy functional (62) is *identical* with the energy functional (30) of conventional density functional theory: By

virtue of the HK theorem the orbitals  $\{\varphi_j\}$  are functionals of the density  $n$  so that

$$E_v[n] = E^{\text{OPM}}[\{\varphi_j[n]\}] \quad . \quad (67)$$

In other words, the orbital functional (62) is an *implicit* density functional. If the (unknown) exact xc functional were used in Eq. (62) then the optimized effective potential determined by Eqs. (65) and (66) would be the exact KS potential. Any approximation of  $E_{xc}$  used in Eq. (62), on the other hand, leads to an approximate KS potential.

There are three non-trivial density functionals contributing to the total-energy functional (30): the non-interacting kinetic-energy functional  $T_s[n]$ , the exchange part  $E_x[n]$  and the correlation part  $E_c[n]$  of  $E_{xc}[n]$ . If  $T_s[n]$  is approximated by the gradient expansion (54) one obtains the Thomas-Fermi model and its extensions. The transition from Thomas-Fermi to modern KS theory is equivalent to replacing the *approximate* functional (54) by the *exact orbital representation*

$$T_s^{\text{exact}}[n] = \sum_{j=1}^N \int d^3r \varphi_j^*[n](\mathbf{r}) \left( -\frac{\hbar^2 \nabla^2}{2m} \right) \varphi_j[n](\mathbf{r}) \quad . \quad (68)$$

The transition from standard KS theory to the OPM can be viewed in much the same way: While in ordinary KS theory the exchange-energy functional is *approximated* by LDA or GGA-type functionals [see Eq. (55) and Eq. (57)], the OPM employs the *exact orbital representation*

$$E_x^{\text{exact}} = -\frac{e^2}{2} \sum_{i,j=1}^N \delta_{\sigma_i \sigma_j} \int d^3r \int d^3r' \frac{\varphi_i^*[n](\mathbf{r}') \varphi_j[n](\mathbf{r}') \varphi_i[n](\mathbf{r}) \varphi_j^*[n](\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad . \quad (69)$$

As a consequence,  $v_x^{\text{OPM}}$  is manifestly self-interaction free. Of course, the correlation part  $E_c[n]$  still has to be approximated, but even for  $E_c[n]$  the representation in terms of orbitals allows more flexibility in the construction of approximate functionals. In particular,  $v_{xc}^{\text{OPM}}$  is currently the only approximate xc potential featuring the required discontinuities as a function of the particle number  $N$  (Krieger *et al.* 1992).

The full OPM, however, has a serious drawback: The solution of the integral equation (65) is numerically very involved. Recently, Krieger, Li, and Iafrate (KLI) (1992) proposed an approximate *analytical* solution of the integral equation (65), in which  $v_x^{\text{OPM}}(\mathbf{r})$  is essentially obtained from the solution of a linear ( $N \times N$ ) equation. They also showed that in the x-only case the results of the KLI approximation are nearly identical with those of the exact OPM (Talman and Shadwick 1976; Norman and Koelling 1984; Engel *et al.* 1992; Engel and Vosko 1993a, 1993b). In addition, the KLI approximation preserves all of the important advantages of the exact OPM, such as the correct asymptotic  $-\frac{e^2}{r}$  decay of  $v_{xc}^{\text{OPM}}(\mathbf{r})$  and the discontinuities of  $v_{xc}^{\text{OPM}}(\mathbf{r})$  as a function of the particle number.

The OPM in the KLI approximation has recently been applied (Grabo and Gross 1995; Gross *et al.* 1996) using a correlation energy functional developed by Colle and Salvetti (1975, 1979). The resulting atomic ground state energies are given in Table 1. The mean absolute deviation of  $\bar{\Delta} = 4.7\text{mH}$  is much better than for the GGAs; in fact, the accuracy is comparable with recent CI results ( $\bar{\Delta} = 4.5\text{mH}$ ).

To summarize our overview up to this point, the existence theorems of HK and KS are fairly easy to prove. The harder part of density functional theory is the construction of appropriate approximations of the xc functional. Even for the simplest possible approximation, the LDA, a lot of theoretical work on the homogeneous electron gas was involved: One needs the high-density limit first treated by Gell-Mann and Brueckner (1957), one needs the low-density limit known as the Wigner crystal (Wigner 1934, 1938) and, for the intermediate density regime, quantum Monte Carlo computations (Ceperley and Alder 1980) and/or many-body perturbation theory beyond RPA (Bishop and Lührmann 1978, 1982) is required. Finally, all these data have to be put together in a reliable parametrization (Vosko *et al.* 1980; Perdew and Zunger 1981). The construction of functionals containing gradients of the density is even harder as can be seen from the long list of papers quoted above. However, once a reliable approximation of  $E_{xc}[n]$  has been found, the numerical implementation of the KS scheme is rather simple, at least in comparison with other methods such as CI or diagrammatic many-body techniques. The crucial advantage of density functional theory is its numerical simplicity, allowing the treatment of large inhomogeneous systems for which the traditional methods of quantum chemistry are prohibitively time-consuming.

## 4 Hohenberg-Kohn-Sham formalism for superconducting systems

Let us now consider the grand canonical Hamiltonian for a superconducting system coupled to an electron reservoir with fixed chemical potential  $\mu$  and subject to the external potentials  $v_{ext}(\mathbf{r})$  and  $D_{ext}(\mathbf{r}, \mathbf{r}')$ . The Coulomb potential  $v_{ext}(\mathbf{r})$  is caused by the ions of a crystal lattice, and the complex pairing potential  $D_{ext}(\mathbf{r}, \mathbf{r}')$  can be viewed as being induced by the proximity of an adjacent superconductor. In second quantization, the Hamiltonian reads as follows:

$$\begin{aligned} \hat{H} = & \hat{T} + \hat{U} + \hat{W} + \sum_{\sigma=\uparrow\downarrow} \int d^3r (v_{ext}(\mathbf{r}) - \mu) \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}) \\ & - \int d^3r \int d^3r' (D_{ext}^*(\mathbf{r}, \mathbf{r}') \hat{\psi}_{\uparrow}(\mathbf{r}) \hat{\psi}_{\downarrow}(\mathbf{r}') + D_{ext}(\mathbf{r}, \mathbf{r}') \hat{\psi}_{\downarrow}^{\dagger}(\mathbf{r}') \hat{\psi}_{\uparrow}^{\dagger}(\mathbf{r})) \quad , \quad (70) \end{aligned}$$

where  $\hat{T}$  and  $\hat{U}$  are given by Eqs. (2) and (4), respectively, and

$$\hat{W} = - \int d^3 r_1 \int d^3 r'_1 \int d^3 r_2 \int d^3 r'_2 \hat{\psi}_\downarrow^\dagger(\mathbf{r}_1) \hat{\psi}_\uparrow^\dagger(\mathbf{r}'_1) w(\mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}'_2) \hat{\psi}_\uparrow(\mathbf{r}_2) \hat{\psi}_\downarrow(\mathbf{r}'_2) \quad (71)$$

denotes a phonon-induced electron-electron interaction (written in its general, completely nonlocal form). As a special case we mention the well-known BCS interaction which depends only on the relative coordinates and a typical phonon frequency  $\omega_D$ :

$$w_{\text{BCS}}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{r}_3 - \mathbf{r}_4) = \int \frac{d^3 q}{(2\pi)^3} \int \frac{d^3 p}{(2\pi)^3} e^{i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} e^{i\mathbf{q}(\mathbf{r}_3 - \mathbf{r}_4)} w_{qp} \quad (72)$$

with

$$w_{qp} = \begin{cases} \lambda & \text{if } |\frac{\hbar^2 q^2}{2m} - \mu| < \hbar\omega_D \quad \text{and} \quad |\frac{\hbar^2 p^2}{2m} - \mu| < \hbar\omega_D \\ 0 & \text{otherwise.} \end{cases} \quad (73)$$

The HK theorem for superconductors is now formulated (Oliveira *et al.* 1988) analogously to the theorem for normal-state many-electron systems discussed in section 2. In addition to the normal ground state density

$$n(\mathbf{r}) = \sum_{\sigma=\uparrow\downarrow} \langle \hat{\psi}_\sigma^\dagger(\mathbf{r}) \hat{\psi}_\sigma(\mathbf{r}) \rangle \quad (74)$$

we need the anomalous density

$$\Delta(\mathbf{r}, \mathbf{r}') = \langle \hat{\psi}_\uparrow(\mathbf{r}) \hat{\psi}_\downarrow(\mathbf{r}') \rangle \quad , \quad (75)$$

whose diagonal  $\Delta(\mathbf{r}, \mathbf{r})$  is identical with the order parameter of the Ginzburg-Landau theory (Ginzburg and Landau 1950) (in the appropriate limits). The HK theorem states that there exists a one-to-one mapping between the pair of ground state densities  $[n(\mathbf{r}), \Delta(\mathbf{r}, \mathbf{r}')]$  and the pair of potentials  $[v_{ext}(\mathbf{r}) - \mu, D_{ext}(\mathbf{r}, \mathbf{r}')]$ . Therefore, the ground state expectation value of each physical variable can be written as a functional of the two densities. As in the normal-state case, a variational principle can be established which states that the exact ground state densities are obtained from the Euler-Lagrange equations

$$\frac{\delta E[n, \Delta]}{\delta n(\mathbf{r})} = 0 \quad (76)$$

and

$$\frac{\delta E[n, \Delta]}{\delta \Delta^*(\mathbf{r}, \mathbf{r}')} = 0 \quad (77)$$

with suitable boundary conditions, where

$$\begin{aligned} E[n, \Delta] = & T_s[n, \Delta] + \int d^3 r (v_{ext}(\mathbf{r}) - \mu)n(\mathbf{r}) + \frac{e^2}{2} \int d^3 r \int d^3 r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ & - \int d^3 r \int d^3 r' (D_{ext}^*(\mathbf{r}, \mathbf{r}')\Delta(\mathbf{r}, \mathbf{r}') + D_{ext}(\mathbf{r}, \mathbf{r}')\Delta^*(\mathbf{r}, \mathbf{r}')) \\ & - \int d^3 r_1 \int d^3 r'_1 \int d^3 r_2 \int d^3 r'_2 \Delta^*(\mathbf{r}_1, \mathbf{r}'_1) w(\mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}'_2) \Delta(\mathbf{r}_2, \mathbf{r}'_2) + E_{xc}[n, \Delta] \quad . \quad (78) \end{aligned}$$

Here,  $T_s[n, \Delta]$  is the functional of the kinetic energy of a non-interacting system with densities  $n$  and  $\Delta$ , and the xc energy functional  $E_{xc}[n, \Delta]$  is formally given by

$$E_{xc}[n, \Delta] = F[n, \Delta] - \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \int d^3r_1 \int d^3r'_1 \int d^3r_2 \int d^3r'_2 \Delta^*(\mathbf{r}_1, \mathbf{r}'_1) w(\mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}'_2) \Delta(\mathbf{r}_2, \mathbf{r}'_2) - T_s[n, \Delta] \quad . \quad (79)$$

The universal functional  $F[n, \Delta]$  is defined in analogy to Eq. (23).

Following the normal-state KS formalism (section 2) in making the assumption of non-interacting  $v$ -representability, the calculation of the densities can be performed via construction of a non-interacting system with effective potentials  $v_s(\mathbf{r})$  and  $D_s(\mathbf{r}, \mathbf{r}')$  which yields the same densities  $n(\mathbf{r})$  and  $\Delta(\mathbf{r}, \mathbf{r}')$  as the fully interacting system described by the Hamiltonian (70). One can then establish a set of single-particle equations for the non-interacting system:

$$\left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) - \mu \right) u_k(\mathbf{r}) + \int d^3r' D_s(\mathbf{r}, \mathbf{r}') v_k(\mathbf{r}') = E_k u_k(\mathbf{r}) \quad (80)$$

$$-\left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) - \mu \right) v_k(\mathbf{r}) + \int d^3r' D_s^*(\mathbf{r}, \mathbf{r}') u_k(\mathbf{r}') = E_k v_k(\mathbf{r}) \quad . \quad (81)$$

In terms of the particle and hole amplitudes,  $u_k(\mathbf{r})$  and  $v_k(\mathbf{r})$ , the densities are given by

$$n(\mathbf{r}) = 2 \sum_k [|u_k(\mathbf{r})|^2 \theta(-E_k) + |v_k(\mathbf{r})|^2 \theta(E_k)] \quad (82)$$

$$\Delta(\mathbf{r}, \mathbf{r}') = \sum_k [v_k^*(\mathbf{r}') u_k(\mathbf{r}) \theta(E_k) - v_k^*(\mathbf{r}) u_k(\mathbf{r}') \theta(-E_k)] \quad , \quad (83)$$

where  $\theta(E)$  denotes the usual step function (0 for  $E < 0$  and 1 for  $E > 0$ ). The effective potentials appearing in Eqs. (80) and (81) are functionals of the two densities:

$$v_s[n, \Delta](\mathbf{r}) = v_{ext}(\mathbf{r}) + e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n, \Delta](\mathbf{r}) \quad (84)$$

$$D_s[n, \Delta](\mathbf{r}, \mathbf{r}') = D_{ext}(\mathbf{r}, \mathbf{r}') + \int d^3r_2 \int d^3r'_2 w(\mathbf{r}, \mathbf{r}', \mathbf{r}_2, \mathbf{r}'_2) \Delta(\mathbf{r}_2, \mathbf{r}'_2) + D_{xc}[n, \Delta](\mathbf{r}, \mathbf{r}') \quad (85)$$

where

$$v_{xc}[n, \Delta](\mathbf{r}) = \frac{\delta E_{xc}[n, \Delta]}{n(\mathbf{r})} \quad (86)$$

$$D_{xc}[n, \Delta](\mathbf{r}, \mathbf{r}') = -\frac{\delta E_{xc}[n, \Delta]}{\Delta^*(\mathbf{r}, \mathbf{r}')} \quad . \quad (87)$$

Since  $v_s$  and  $D_s$  depend on the densities, the whole set of equations (80)–(87) has to be solved self-consistently. Eqs. (80) and (81) bear structural resemblance to the Bogoliubov-de Gennes equations (de Gennes 1966), but – in contrast to the latter – include xc effects in principle exactly.

In superconductors most quantities of physical interest depend critically on temperature. A finite-temperature version of the above ground-state formalism is easily established (Oliveira *et al.* 1988) in analogy to the finite-temperature extension (Mermin 1965) of ordinary density functional theory. The structure of the self-consistent equations (80)–(87) remains the same at finite temperature; only the xc potentials (86) and (87) depend on the temperature both explicitly through the functional and implicitly through the densities which have to be calculated by substituting the Fermi distribution  $f(E) = [1 + \exp(E/k_B T)]^{-1}$  for the step function  $\theta(E)$  in Eqs. (82) and (83).

As in ordinary density functional theory, the construction of approximations of the functionals involved is the crucial step on the way towards explicit applications. In the following sections we shall investigate the gradient expansion for superconductors. We restrict ourselves to the simplest possible case: the kinetic-energy functional  $T_s[n, \Delta]$  at zero temperature. In section 5, the semiclassical expansion required for the gradient expansion is performed for the general case of complex-valued pairing fields. Real-valued pairing fields have previously been treated by Taruishi and Schuck (1992). In section 6 the density-gradient expansion of  $T_s[n, \Delta]$  is constructed from the semiclassical expansion. The procedure is easily generalized to finite temperature. Explicit results for the gradient expansion of the exchange-energy functionals of superconductors at finite temperature will be presented elsewhere.

## 5 Semiclassical expansion for superconductors

### 5.1 Green's functions for the non-interacting system

We consider a non-interacting system described by the single-particle Hamiltonian

$$\begin{aligned} \hat{H}_s = & \sum_{\sigma=\uparrow\downarrow} \int d^3r \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{r}) - \mu \right) \hat{\psi}_\sigma(\mathbf{r}) \\ & - \int d^3r \int d^3r' (D_s^*(\mathbf{r}, \mathbf{r}') \hat{\psi}_\uparrow(\mathbf{r}) \hat{\psi}_\downarrow(\mathbf{r}') + D_s(\mathbf{r}, \mathbf{r}') \hat{\psi}_\downarrow^\dagger(\mathbf{r}') \hat{\psi}_\uparrow^\dagger(\mathbf{r})) \quad . \end{aligned} \quad (88)$$

The system described by this Hamiltonian is superconducting due to the pairing potential  $D_s(\mathbf{r}, \mathbf{r}')$ . The single-particle potentials  $v_s(\mathbf{r})$  and  $D_s(\mathbf{r}, \mathbf{r}')$  may but need not be the KS potentials of a particular interacting system.

In the following we shall determine the normal and anomalous one-particle Green's functions corresponding to this Hamiltonian. For this purpose we need two commutator relations:

$$[\hat{\psi}_\sigma(\mathbf{x}), \hat{H}_s] = \left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{x}) - \mu \right) \hat{\psi}_\sigma(\mathbf{x}) - \alpha \int d^3r D_s(\mathbf{r}, \mathbf{x}) \hat{\psi}_{-\sigma}^\dagger(\mathbf{r}) \quad (89)$$

$$[\hat{\psi}_\sigma^\dagger(\mathbf{x}), \hat{H}_s] = -\hat{\psi}_\sigma^\dagger(\mathbf{x}) \left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{x}) - \mu \right) + \alpha \int d^3r D_s^*(\mathbf{r}, \mathbf{x}) \hat{\psi}_{-\sigma}(\mathbf{r}) \quad (90)$$

where

$$\alpha = \begin{cases} -1 & \text{for } \sigma = \uparrow \\ +1 & \text{for } \sigma = \downarrow \end{cases} . \quad (91)$$

Next we switch to the Heisenberg picture and use (89) and (90) to set up the Heisenberg equations of motion for the field operators:

$$i\hbar \frac{\partial}{\partial t} \hat{\psi}_\sigma(\mathbf{x}t)_\text{H} = \left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{x}) - \mu \right) \hat{\psi}_\sigma(\mathbf{x}t)_\text{H} - \alpha \int d^3r D_s(\mathbf{r}, \mathbf{x}) \hat{\psi}_{-\sigma}^\dagger(\mathbf{r}t)_\text{H} \quad (92)$$

$$i\hbar \frac{\partial}{\partial t} \hat{\psi}_\sigma^\dagger(\mathbf{x}t)_\text{H} = -\hat{\psi}_\sigma^\dagger(\mathbf{x}t)_\text{H} \left( -\frac{\hbar^2 \nabla^2}{2m} + v_s(\mathbf{x}) - \mu \right) + \alpha \int d^3r D_s^*(\mathbf{r}, \mathbf{x}) \hat{\psi}_{-\sigma}(\mathbf{r}t)_\text{H} . \quad (93)$$

The normal one-particle Green's function is defined as

$$\mathcal{G}_{\sigma\sigma'}(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{i} \langle T[\hat{\psi}_\sigma(\mathbf{x}t)_\text{H} \hat{\psi}_{\sigma'}^\dagger(\mathbf{x}'t')_\text{H}] \rangle \quad (94)$$

where  $T$  denotes the usual time-ordered product

$$T[A(t)B(t')] = \begin{cases} A(t)B(t') & \text{for } t > t' \\ -B(t')A(t) & \text{for } t' > t \end{cases} . \quad (95)$$

It is easy to see that  $\mathcal{G}_{\sigma\sigma'}(\mathbf{x}t, \mathbf{x}'t') = \delta_{\sigma\sigma'} \mathcal{G}(\mathbf{x}t, \mathbf{x}'t')$  where

$$\mathcal{G}(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{i} \langle T[\hat{\psi}_\uparrow(\mathbf{x}t)_\text{H} \hat{\psi}_\uparrow^\dagger(\mathbf{x}'t')_\text{H}] \rangle = \frac{1}{i} \langle T[\hat{\psi}_\downarrow(\mathbf{x}t)_\text{H} \hat{\psi}_\downarrow^\dagger(\mathbf{x}'t')_\text{H}] \rangle . \quad (96)$$

We then define the anomalous Green's functions as:

$$\mathcal{F}(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{i} \langle T[\hat{\psi}_\uparrow(\mathbf{x}t)_\text{H} \hat{\psi}_\downarrow(\mathbf{x}'t')_\text{H}] \rangle \quad (97)$$

$$\mathcal{F}^\dagger(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{i} \langle T[\hat{\psi}_\downarrow^\dagger(\mathbf{x}t)_\text{H} \hat{\psi}_\uparrow^\dagger(\mathbf{x}'t')_\text{H}] \rangle . \quad (98)$$

In order to obtain equations of motion for the Green's functions given above we have to compute their derivatives with respect to time. Expressing the time-ordered products in terms of the step function  $\theta(t - t')$ , we find

$$\frac{\partial}{\partial t} \mathcal{G}(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{i} \delta(t - t') \delta(\mathbf{x} - \mathbf{x}') + \frac{1}{i} \langle T[\frac{\partial}{\partial t} \hat{\psi}_\uparrow(\mathbf{x}t) \hat{\psi}_\uparrow^\dagger(\mathbf{x}'t')] \rangle \quad (99)$$

$$\frac{\partial}{\partial t} \mathcal{G}(\mathbf{x}'t', \mathbf{x}t) = -\frac{1}{i} \delta(t - t') \delta(\mathbf{x} - \mathbf{x}') - \frac{1}{i} \langle T[\frac{\partial}{\partial t} \hat{\psi}_\uparrow^\dagger(\mathbf{x}t) \hat{\psi}_\uparrow(\mathbf{x}'t')] \rangle \quad (100)$$

$$\frac{\partial}{\partial t} \mathcal{F}(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{i} \langle T[\frac{\partial}{\partial t} \hat{\psi}_\uparrow(\mathbf{x}t) \hat{\psi}_\downarrow(\mathbf{x}'t')] \rangle \quad (101)$$

$$\frac{\partial}{\partial t} \mathcal{F}^\dagger(\mathbf{x}t, \mathbf{x}'t') = \frac{1}{i} \langle T[\frac{\partial}{\partial t} \hat{\psi}_\downarrow^\dagger(\mathbf{x}t) \hat{\psi}_\uparrow^\dagger(\mathbf{x}'t')] \rangle \quad (102)$$

where we have used the anticommutator relations for fermionic field operators. Here and in the following, the index ‘‘H’’ denoting the Heisenberg picture is dropped for notational simplicity.

We now insert the equations of motion (92) and (93) into (99)–(102) and are thus led to a set of four coupled equations for the Green's functions:

$$\left(i\hbar\frac{\partial}{\partial t} - \left(-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu\right)\right) \mathcal{G}(\mathbf{x}t, \mathbf{x}'t') - \int d^3r D_s(\mathbf{r}, \mathbf{x}) \mathcal{F}^\dagger(\mathbf{r}t, \mathbf{x}'t') = \hbar\delta(t-t')\delta(\mathbf{x}-\mathbf{x}') \quad (103)$$

$$- \left(i\hbar\frac{\partial}{\partial t} + \left(-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu\right)\right) \mathcal{G}(\mathbf{x}'t', \mathbf{x}t) - \int d^3r D_s^*(\mathbf{r}, \mathbf{x}) \mathcal{F}(\mathbf{r}t, \mathbf{x}'t') = \hbar\delta(t-t')\delta(\mathbf{x}-\mathbf{x}') \quad (104)$$

$$\left(i\hbar\frac{\partial}{\partial t} - \left(-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu\right)\right) \mathcal{F}(\mathbf{x}t, \mathbf{x}'t') + \int d^3r D_s(\mathbf{r}, \mathbf{x}) \mathcal{G}_{\sigma\sigma'}(\mathbf{x}'t', \mathbf{r}t) = 0 \quad (105)$$

$$\left(i\hbar\frac{\partial}{\partial t} + \left(-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu\right)\right) \mathcal{F}^\dagger(\mathbf{x}t, \mathbf{x}'t') - \int d^3r D_s^*(\mathbf{r}, \mathbf{x}) \mathcal{G}_{\sigma\sigma'}(\mathbf{r}t, \mathbf{x}'t') = 0 \quad (106)$$

In the next step we make use of the fact that the Hamiltonian (88) is manifestly independent of time. Hence the Green's functions  $\mathcal{G}$  and  $\mathcal{F}$  can be shown to depend only on the difference  $(t-t')$ , and we can go over to the Fourier representation

$$\mathcal{G}(\mathbf{x}, \mathbf{x}', \omega) = \int d(t-t') e^{\frac{i}{\hbar}\omega(t-t')} \mathcal{G}(\mathbf{x}t, \mathbf{x}'t') \quad (107)$$

with the inverse

$$\mathcal{G}(\mathbf{x}t, \mathbf{x}'t') = \int \frac{d\omega}{2\pi\hbar} e^{-\frac{i}{\hbar}\omega(t-t')} \mathcal{G}(\mathbf{x}, \mathbf{x}', \omega) \quad (108)$$

It should be noted that here and in the following,  $\omega$  always denotes an *energy* (rather than a frequency). Fourier transformation of the relations (103)–(106) leads to

$$\left(\omega - \left(-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu\right)\right) \mathcal{G}(\mathbf{x}, \mathbf{x}', \omega) - \int d^3r D_s(\mathbf{r}, \mathbf{x}) \mathcal{F}^\dagger(\mathbf{r}, \mathbf{x}', \omega) = \hbar\delta(\mathbf{x}-\mathbf{x}') \quad (109)$$

$$- \left(\omega + \left(-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu\right)\right) \mathcal{G}(\mathbf{x}', \mathbf{x}, -\omega) - \int d^3r D_s^*(\mathbf{r}, \mathbf{x}) \mathcal{F}(\mathbf{r}, \mathbf{x}', \omega) = \hbar\delta(\mathbf{x}-\mathbf{x}') \quad (110)$$

$$\left(\omega - \left(-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu\right)\right) \mathcal{F}(\mathbf{x}, \mathbf{x}', \omega) + \int d^3r D_s(\mathbf{r}, \mathbf{x}) \mathcal{G}(\mathbf{x}', \mathbf{r}, -\omega) = 0 \quad (111)$$

$$\left(\omega + \left(-\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu\right)\right) \mathcal{F}^\dagger(\mathbf{x}, \mathbf{x}', \omega) - \int d^3r D_s^*(\mathbf{r}, \mathbf{x}) \mathcal{G}(\mathbf{r}, \mathbf{x}', \omega) = 0 \quad (112)$$

In the following it will turn out to be favourable to write Eqs. (109)–(112) in a compact matrix form. For this purpose we define the two-dimensional Green's function (Nambu 1960) as

$$\mathbf{G}(\mathbf{x}, \mathbf{x}', \omega) = \begin{pmatrix} \mathcal{G}(\mathbf{x}, \mathbf{x}', \omega) & \mathcal{F}(\mathbf{x}, \mathbf{x}', \omega) \\ \mathcal{F}^\dagger(\mathbf{x}, \mathbf{x}', \omega) & -\mathcal{G}(\mathbf{x}', \mathbf{x}, -\omega) \end{pmatrix}, \quad (113)$$

and with the substitution

$$h(\mathbf{x}) = -\frac{\hbar^2\nabla^2}{2m} + v_s(\mathbf{x}) - \mu \quad (114)$$

and the two-dimensional unit matrix  $\mathbf{I}$  we finally obtain

$$\int d^3r \begin{pmatrix} \delta(\mathbf{r}-\mathbf{x})(\omega - h(\mathbf{r})) & -D_s(\mathbf{r}, \mathbf{x}) \\ -D_s^*(\mathbf{r}, \mathbf{x}) & \delta(\mathbf{r}-\mathbf{x})(\omega + h(\mathbf{r})) \end{pmatrix} \mathbf{G}(\mathbf{r}, \mathbf{x}', \omega) = \hbar\mathbf{I}\delta(\mathbf{x}-\mathbf{x}') \quad (115)$$



## 5.2 The Wigner transformation

As mentioned in the introduction, it is favourable to choose the mixed representation  $\Delta(\mathbf{R}, \mathbf{p})$  for the superconducting order parameter, i. e., the Wigner transform of  $\Delta(\mathbf{r}, \mathbf{r}')$ . This will eventually allow us to calculate the density-gradient expansion of  $T_s[n, \Delta]$  in systematic manner. With the coordinate transformation

$$\mathbf{R} = \frac{\mathbf{r} + \mathbf{r}'}{2} \quad \mathbf{s} = \mathbf{r} - \mathbf{r}' \quad (116)$$

and its inverse

$$\mathbf{r} = \mathbf{R} + \frac{\mathbf{s}}{2} \quad \mathbf{r}' = \mathbf{R} - \frac{\mathbf{s}}{2} \quad (117)$$

it follows that each quantity depending on  $\mathbf{r}$  and  $\mathbf{r}'$  can alternatively be written as a function of  $\mathbf{R}$  and  $\mathbf{s}$ :

$$f(\mathbf{r}, \mathbf{r}') = f(\mathbf{r}(\mathbf{R}, \mathbf{s}), \mathbf{r}'(\mathbf{R}, \mathbf{s})) = f(\mathbf{R}, \mathbf{s}) \quad . \quad (118)$$

For simplicity we use the same symbol,  $f$ , for the function  $f(\mathbf{r}, \mathbf{r}')$  and the function  $f(\mathbf{R}, \mathbf{s})$ . The Wigner transform (Wigner 1932) of  $f(\mathbf{R}, \mathbf{s})$  is defined as the function

$$f_w(\mathbf{R}, \mathbf{p}) = \int d^3 s e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{s}} f(\mathbf{R}, \mathbf{s}) \quad . \quad (119)$$

The inverse transformation is

$$f(\mathbf{R}, \mathbf{s}) = \int \frac{d^3 p}{(2\pi\hbar)^3} e^{-\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{s}} f_w(\mathbf{R}, \mathbf{p}) \quad . \quad (120)$$

In this context, two relations can be shown to hold:

$$\int d^3 r \int d^3 r' f(\mathbf{r}, \mathbf{r}') = \int d^3 R \int d^3 s f(\mathbf{R}, \mathbf{s}) \quad (121)$$

$$\int d^3 r \int d^3 r' f(\mathbf{r}, \mathbf{r}') g(\mathbf{r}, \mathbf{r}') = \int d^3 R \int \frac{d^3 p}{(2\pi\hbar)^3} f_w(\mathbf{R}, \pm \mathbf{p}) g_w(\mathbf{R}, \mp \mathbf{p}) \quad . \quad (122)$$

In the following we shall express the total-energy functional (78) in terms of the Wigner-transformed densities. For this purpose we make use of some properties of the pairing interaction and the order parameter: The hermiticity of (71) requires that

$$w(\mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}'_2) = w^*(\mathbf{r}'_2, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}_1) \quad , \quad (123)$$

and spin isotropy implies

$$w(\mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}'_2) = w(\mathbf{r}'_1, \mathbf{r}_1, \mathbf{r}'_2, \mathbf{r}_2) \quad . \quad (124)$$

Gross and Kurth (1991) have shown that

$$\Delta(\mathbf{r}, \mathbf{r}') = \Delta(\mathbf{r}', \mathbf{r}) \quad (125)$$

$$D_{ext}(\mathbf{r}, \mathbf{r}') = D_{ext}(\mathbf{r}', \mathbf{r}) \quad . \quad (126)$$

The corresponding relations of the Wigner transforms are

$$\Delta_w(\mathbf{R}, \mathbf{p}) = \Delta_w(\mathbf{R}, -\mathbf{p}) \quad (127)$$

$$D_{ext_w}(\mathbf{R}, \mathbf{p}) = D_{ext_w}(\mathbf{R}, -\mathbf{p}) \quad (128)$$

$$w_w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}') = w_w(\mathbf{R}, -\mathbf{p}, \mathbf{R}', -\mathbf{p}') \quad (129)$$

$$w_w^*(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}') = w_w(\mathbf{R}', \mathbf{p}', \mathbf{R}, \mathbf{p}) \quad (130)$$

where  $w_w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}')$  stands for a double Wigner transform:

$$w_w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}') = \int d^3 s \int d^3 s' e^{\frac{i}{\hbar} \mathbf{p} \cdot \mathbf{s}} e^{\frac{i}{\hbar} \mathbf{p}' \cdot \mathbf{s}'} w(\mathbf{R}, \mathbf{s}, \mathbf{R}', \mathbf{s}') \quad . \quad (131)$$

The formulas given above enable us to express the energy functional (78) by transformed quantities. From now on we shall suppress the index “w”; the Wigner transform is implied by the arguments  $(\mathbf{R}, \mathbf{p})$ . We thus obtain

$$\begin{aligned} E[n, \Delta] = & T_s[n, \Delta] + \int d^3 R (v_{ext}(\mathbf{R}) - \mu) n(\mathbf{R}) + \frac{e^2}{2} \int d^3 R \int d^3 R' \frac{n(\mathbf{R}) n(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} \\ & - \int d^3 R \int \frac{d^3 p}{(2\pi\hbar)^3} (D_{ext}^*(\mathbf{R}, \mathbf{p}) \Delta(\mathbf{R}, \mathbf{p}) + D_{ext}(\mathbf{R}, \mathbf{p}) \Delta^*(\mathbf{R}, \mathbf{p})) \\ & - \int d^3 R \int \frac{d^3 p}{(2\pi\hbar)^3} \int d^3 R' \int \frac{d^3 p'}{(2\pi\hbar)^3} \Delta^*(\mathbf{R}, \mathbf{p}) w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}') \Delta(\mathbf{R}', \mathbf{p}') + E_{xc}[n, \Delta] \quad . \quad (132) \end{aligned}$$

The Hohenberg-Kohn variational principle is also valid for variations with respect to the densities  $n(\mathbf{R})$  and  $\Delta^*(\mathbf{R}, \mathbf{p})$ ; inserting (132) in (76) and (77) we find the following two variational equations:

$$\frac{\delta T_s[n, \Delta]}{\delta n(\mathbf{R})} = \mu - v_{ext}(\mathbf{R}) - e^2 \int d^3 R' \frac{n(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} - \frac{\delta E_{xc}[n, \Delta]}{\delta n(\mathbf{R})} \quad (133)$$

$$\begin{aligned} (2\pi\hbar)^3 \frac{\delta T_s[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} = & D_{ext}(\mathbf{R}, \mathbf{p}) + \int d^3 R' \int \frac{d^3 p'}{(2\pi\hbar)^3} w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}') \Delta(\mathbf{R}', \mathbf{p}') \\ & - (2\pi\hbar)^3 \frac{\delta E_{xc}[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} \quad . \quad (134) \end{aligned}$$

The two equations above represent a central result of the density functional theory for superconductors in the Hohenberg-Kohn version. They are a pair of coupled integral equations whose solution would yield the ground state densities in principle exactly if the precise form of the functionals  $T_s[n, \Delta]$  and  $E_{xc}[n, \Delta]$  were known.

### 5.3 Method of the semiclassical expansion

If the Wigner transformation is applied to a product of two operators in coordinate representation, say

$$\int d^3 x' A(\mathbf{x}, \mathbf{x}') B(\mathbf{x}', \mathbf{x}'') = C(\mathbf{x}, \mathbf{x}'') \quad , \quad (135)$$

one ends up with

$$\Lambda[A(\mathbf{R}, \mathbf{p}), B(\mathbf{R}', \mathbf{p}')] = C(\mathbf{R}, \mathbf{p}) \quad , \quad (136)$$

where the operator  $\Lambda$  is defined as

$$\begin{aligned} \Lambda[A(\mathbf{R}, \mathbf{p}), B(\mathbf{R}', \mathbf{p}')] &= \\ &= \lim_{\substack{\mathbf{R}' \rightarrow \mathbf{R} \\ \mathbf{p}' \rightarrow \mathbf{p}}} \exp \left[ -\frac{i\hbar}{2} (\nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{p}'} - \nabla_{\mathbf{p}} \cdot \nabla_{\mathbf{R}'}) \right] A(\mathbf{R}, \mathbf{p}) B(\mathbf{R}', \mathbf{p}') \quad . \end{aligned} \quad (137)$$

The above formula is an original result of Theis (1955), a detailed derivation can be found in the work of Baraff and Borowitz (1961). We shall now apply this formula to our problem:

Defining

$$h(\mathbf{R}, \mathbf{p}) = \frac{p^2}{2m} + v_s(\mathbf{R}) - \mu \quad , \quad (138)$$

we obtain the Wigner transform of Eq. (115) in compact matrix form:

$$\Lambda[(\omega \mathbf{I} - \mathbf{H}(\mathbf{R}, \mathbf{p})), \mathbf{G}(\mathbf{R}', \mathbf{p}', \omega)] = \hbar \mathbf{I} \quad (139)$$

with

$$\mathbf{G}(\mathbf{R}, \mathbf{p}, \omega) = \begin{pmatrix} \mathcal{G}(\mathbf{R}, \mathbf{p}, \omega) & \mathcal{F}(\mathbf{R}, \mathbf{p}, \omega) \\ \mathcal{F}^\dagger(\mathbf{R}, \mathbf{p}, \omega) & -\mathcal{G}(\mathbf{R}, -\mathbf{p}, -\omega) \end{pmatrix} \quad (140)$$

and

$$\mathbf{H}(\mathbf{R}, \mathbf{p}) = \begin{pmatrix} h(\mathbf{R}, \mathbf{p}) & D_s(\mathbf{R}, \mathbf{p}) \\ D_s^*(\mathbf{R}, \mathbf{p}) & -h(\mathbf{R}, \mathbf{p}) \end{pmatrix} \quad . \quad (141)$$

We note from (137) that the operator  $\Lambda$  can be written as a series in powers of  $\hbar$ , where the orders of  $\hbar$  correspond to the degree of the derivatives of the quantities acted on by  $\Lambda$ . In other words, the Wigner transform of an integrated product consists of the product of the individual Wigner transforms (i. e., the lowest order term of  $\Lambda$  in  $\hbar$ ) plus products of derivatives of the Wigner transforms (i. e., higher order terms of  $\Lambda$ ). Symbolically we can write the operator  $\Lambda$  in the form

$$\Lambda = \sum_{j=0}^{\infty} \hbar^j \Lambda_j = \sum_{j=0}^{\infty} \frac{\hbar^j}{j!} \lim_{\substack{\mathbf{R}' \rightarrow \mathbf{R} \\ \mathbf{p}' \rightarrow \mathbf{p}}} \left[ -\frac{i\hbar}{2} (\nabla_{\mathbf{R}} \cdot \nabla_{\mathbf{p}'} - \nabla_{\mathbf{p}} \cdot \nabla_{\mathbf{R}'}) \right]^j \quad (142)$$

and introduce a formal expansion of  $\mathbf{G}$  in powers of  $\hbar$ :

$$\mathbf{G}(\mathbf{R}, \mathbf{p}, \omega) = \hbar \sum_{n=0}^{\infty} \mathbf{G}_n(\mathbf{R}, \mathbf{p}, \omega) \hbar^n \quad . \quad (143)$$

We now insert (142) and (143) into (139); separating the orders in  $\hbar$ , we find the following series of equations:

$$\Lambda_0[(\omega\mathbf{I} - \mathbf{H}(\mathbf{R}, \mathbf{p})), \mathbf{G}_0(\mathbf{R}', \mathbf{p}', \omega)] = \mathbf{I} \quad (144)$$

$$\sum_{j=0}^k \Lambda_j[(\omega\mathbf{I} - \mathbf{H}(\mathbf{R}, \mathbf{p})), \mathbf{G}_{k-j}(\mathbf{R}', \mathbf{p}', \omega)] = 0 \quad \text{for } k \geq 1 \quad . \quad (145)$$

In principle we are now able to determine the solution for  $\mathbf{G}$  in any order of  $\hbar$ , starting with the zeroth order from Eq. (144) and successively calculating the higher orders with (145). Two remarks should be added, however: first, the computational effort involved is very large, even for low orders. On the other hand, we have to keep in mind that our final goal is to develop a gradient expansion for the kinetic energy out of the series representation for the Green's functions. Although there are no rigorous mathematical statements available on the structure of gradient expansions, it is nevertheless known (Dreizler and Gross 1990) that they exhibit the behavior of asymptotic series and therefore cannot be expected to converge; truncation after a few terms, however, normally leads to remarkably good results.

In this paper we take the expansion up to second order in  $\hbar$ , i. e., we calculate  $\mathbf{G}_0$ ,  $\mathbf{G}_1$  and  $\mathbf{G}_2$ . From (144) and (145) the explicit relations used to determine the Green's functions can be written as

$$(\omega\mathbf{I} - \mathbf{H})\mathbf{G}_0 = \mathbf{I} \quad (146)$$

$$(\omega\mathbf{I} - \mathbf{H})\mathbf{G}_1 - \frac{i}{2} \left\{ \nabla_R(\omega\mathbf{I} - \mathbf{H}) \cdot \nabla_p \mathbf{G}_0 - \nabla_p(\omega\mathbf{I} - \mathbf{H}) \cdot \nabla_R \mathbf{G}_0 \right\} = 0 \quad (147)$$

$$\begin{aligned} & (\omega\mathbf{I} - \mathbf{H})\mathbf{G}_2 - \frac{i}{2} \left\{ \nabla_R(\omega\mathbf{I} - \mathbf{H}) \cdot \nabla_p \mathbf{G}_1 - \nabla_p(\omega\mathbf{I} - \mathbf{H}) \cdot \nabla_R \mathbf{G}_1 \right\} \\ & - \frac{1}{8} \sum_{i,k=1}^3 \left\{ \partial_{R_i R_k}^2 (\omega\mathbf{I} - \mathbf{H}) \partial_{p_i p_k}^2 \mathbf{G}_0 + \partial_{p_i p_k}^2 (\omega\mathbf{I} - \mathbf{H}) \partial_{R_i R_k}^2 \mathbf{G}_0 \right. \\ & \quad \left. - 2 \partial_{R_i p_k}^2 (\omega\mathbf{I} - \mathbf{H}) \partial_{p_i R_k}^2 \mathbf{G}_0 \right\} = 0 \quad . \quad (148) \end{aligned}$$

#### 5.4 Calculation of the densities from the Green's functions

Before we start to explicitly compute the semiclassical expansion of the Green's functions, we have to think about how to obtain from them the quantities we are interested in: the densities  $n(\mathbf{R})$  and  $\Delta(\mathbf{R}, \mathbf{p})$  and the kinetic energy density  $t_s(\mathbf{R})$ . Essential for  $n$  and  $t_s$  is the Wigner transform  $\gamma(\mathbf{R}, \mathbf{p})$  of the density matrix, as can be seen from the expressions

$$n(\mathbf{R}) = 2 \int \frac{d^3 p}{(2\pi\hbar)^3} \gamma(\mathbf{R}, \mathbf{p}) \quad (149)$$

and

$$t_s(\mathbf{R}) = \frac{\hbar^2}{2m} \frac{\nabla^2}{4} n(\mathbf{R}) + 2 \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} \gamma(\mathbf{R}, \mathbf{p}) \quad , \quad (150)$$

where (150) follows in a straightforward way from the definition of the non-interacting kinetic energy density

$$t_s(\mathbf{x}) = 2 \frac{\hbar^2}{2m} \nabla_x \cdot \nabla_{x'} \gamma(\mathbf{x}, \mathbf{x}') \Big|_{\mathbf{x}=\mathbf{x}'} \quad (151)$$

with the factor of two resulting from the summation over spins. The kinetic energy  $T_s$  is then given by

$$T_s = \int d^3R t_s(\mathbf{R}) \quad . \quad (152)$$

To determine  $\gamma(\mathbf{R}, \mathbf{p})$ , we start with the definition of the density matrix for spin-up electrons in coordinate representation:

$$\gamma(\mathbf{r}, \mathbf{r}') = \langle \hat{\psi}_\uparrow^\dagger(\mathbf{r}') \hat{\psi}_\uparrow(\mathbf{r}) \rangle \quad . \quad (153)$$

Comparison with the definition of the Green's function (96) leads to

$$\gamma(\mathbf{r}, \mathbf{r}') = -i \lim_{\substack{t' \rightarrow t \\ t' > t}} \mathcal{G}(\mathbf{r}0, \mathbf{r}'(t' - t)) \quad (154)$$

because  $\mathcal{G}$  only depends on the time difference. Furthermore we have

$$\gamma(\mathbf{r}, \mathbf{r}') = -i \lim_{\substack{t' \rightarrow t \\ t' > t}} \int \frac{d\omega}{2\pi\hbar} e^{-\frac{i}{\hbar}\omega(t-t')} \mathcal{G}(\mathbf{r}, \mathbf{r}', \omega) \quad , \quad (155)$$

and for the Wigner transform of (155) we find

$$\gamma(\mathbf{R}, \mathbf{p}) = -\frac{i}{2\pi\hbar} \lim_{\epsilon \rightarrow 0^+} \int d\omega e^{i\omega\epsilon} \mathcal{G}(\mathbf{R}, \mathbf{p}, \omega) \quad . \quad (156)$$

In a similar way we obtain

$$\Delta(\mathbf{R}, \mathbf{p}) = \frac{i}{2\pi\hbar} \lim_{\epsilon \rightarrow 0^-} \int d\omega e^{i\omega\epsilon} \mathcal{F}(\mathbf{R}, \mathbf{p}, \omega) \quad . \quad (157)$$

Hence the expansion (143) of  $\mathbf{G}$  in powers of  $\hbar$  is automatically transferred to  $\gamma$  and  $\Delta$ :

$$\gamma(\mathbf{R}, \mathbf{p}) = \sum_{n=0}^{\infty} \gamma_n(\mathbf{R}, \mathbf{p}) \hbar^n \quad (158)$$

$$\Delta(\mathbf{R}, \mathbf{p}) = \sum_{n=0}^{\infty} \Delta_n(\mathbf{R}, \mathbf{p}) \hbar^n \quad , \quad (159)$$

and thus to  $n$  and  $T_s$ .

We are now confronted with the crucial question of how to carry out the integration over  $\omega$  in both (156) and (157). To find the answer, we first investigate the zero-order Green's functions and, in particular, their dependence on  $\omega$ .

## 5.5 Poles of the zero-order Green's functions

The zero-order Green's functions follow from Eq. (146); we have

$$\mathbf{G}_0 = (\omega\mathbf{I} - \mathbf{H})^{-1} \quad . \quad (160)$$

Calculation of the inverse matrix  $(\omega\mathbf{I} - \mathbf{H})^{-1}$  yields

$$\mathbf{G}_0 = \frac{1}{\omega^2 - h(\mathbf{R}, \mathbf{p})^2 - |D_s(\mathbf{R}, \mathbf{p})|^2} \begin{pmatrix} \omega + h(\mathbf{R}, \mathbf{p}) & D_s(\mathbf{R}, \mathbf{p}) \\ D_s^*(\mathbf{R}, \mathbf{p}) & \omega - h(\mathbf{R}, \mathbf{p}) \end{pmatrix} \quad . \quad (161)$$

Abbreviating  $h(\mathbf{R}, \mathbf{p})$  and  $D_s(\mathbf{R}, \mathbf{p})$  by  $h$  and  $D$ , respectively, we have:

$$\mathcal{G}_0(\mathbf{R}, \mathbf{p}, \omega) = \frac{\omega + h}{\omega^2 - h^2 - |D|^2} \quad (162)$$

$$\mathcal{F}_0(\mathbf{R}, \mathbf{p}, \omega) = \frac{D}{\omega^2 - h^2 - |D|^2} \quad . \quad (163)$$

(162) and (163) can be decomposed into

$$\mathcal{G}_0(\mathbf{R}, \mathbf{p}, \omega) = \frac{1}{2} \frac{1 - \frac{h}{\sqrt{h^2 + |D|^2}}}{\omega + \sqrt{h^2 + |D|^2}} + \frac{1}{2} \frac{1 + \frac{h}{\sqrt{h^2 + |D|^2}}}{\omega - \sqrt{h^2 + |D|^2}} \quad (164)$$

and

$$\mathcal{F}_0(\mathbf{R}, \mathbf{p}, \omega) = -\frac{1}{2} \frac{\frac{D}{\sqrt{h^2 + |D|^2}}}{\omega + \sqrt{h^2 + |D|^2}} + \frac{1}{2} \frac{\frac{D}{\sqrt{h^2 + |D|^2}}}{\omega - \sqrt{h^2 + |D|^2}} \quad . \quad (165)$$

Obviously, both  $\mathcal{G}_0$  and  $\mathcal{F}_0$  have a simple pole at  $\omega = \pm\sqrt{h^2 + |D|^2}$ . The usual method in complex analysis is to infinitesimally shift the poles along the imaginary direction and carry out the integrals (156) and (157) over a closed path in the complex  $\omega$  plane by means of the residue calculus. It can be shown that there exists a unique prescription for shifting the poles, namely to supplement the denominators in (164) and (165) with  $\pm i\eta$  in the following manner:

$$\mathcal{G}_0(\mathbf{R}, \mathbf{p}, \omega) = \lim_{\eta \rightarrow 0^+} \left( \frac{1}{2} \frac{1 - \frac{h}{\sqrt{h^2 + |D|^2}}}{\omega + \sqrt{h^2 + |D|^2} - i\eta} + \frac{1}{2} \frac{1 + \frac{h}{\sqrt{h^2 + |D|^2}}}{\omega - \sqrt{h^2 + |D|^2} + i\eta} \right) \quad (166)$$

$$\mathcal{F}_0(\mathbf{R}, \mathbf{p}, \omega) = \lim_{\eta \rightarrow 0^+} \left( -\frac{1}{2} \frac{\frac{D}{\sqrt{h^2 + |D|^2}}}{\omega + \sqrt{h^2 + |D|^2} - i\eta} + \frac{1}{2} \frac{\frac{D}{\sqrt{h^2 + |D|^2}}}{\omega - \sqrt{h^2 + |D|^2} + i\eta} \right) \quad . \quad (167)$$

These are the desired expressions for the zero-order Green's functions. If we now bring the Green's functions on the main denominator again, we end up with

$$\mathbf{G}_0(\mathbf{R}, \mathbf{p}, \omega) =$$

$$\lim_{\eta \rightarrow 0^+} \frac{1}{\omega^2 - (\sqrt{h^2 + |D|^2} - i\eta)^2} \begin{pmatrix} \omega + h - i\eta \frac{h}{\sqrt{h^2 + |D|^2}} & D - i\eta \frac{D}{\sqrt{h^2 + |D|^2}} \\ D^* - i\eta \frac{D^*}{\sqrt{h^2 + |D|^2}} & \omega - h + i\eta \frac{h}{\sqrt{h^2 + |D|^2}} \end{pmatrix}. \quad (168)$$

From Eq. (160) it then follows that the matrix  $(\omega \mathbf{I} - \mathbf{H})$  has to be written as

$$(\omega \mathbf{I} - \mathbf{H}) = \lim_{\eta \rightarrow 0^+} \begin{pmatrix} \omega - h + i\eta \frac{h}{\sqrt{h^2 + |D|^2}} & -D + i\eta \frac{D}{\sqrt{h^2 + |D|^2}} \\ -D^* + i\eta \frac{D^*}{\sqrt{h^2 + |D|^2}} & \omega + h - i\eta \frac{h}{\sqrt{h^2 + |D|^2}} \end{pmatrix}. \quad (169)$$

We can now proceed and determine  $\mathbf{G}_1$  and  $\mathbf{G}_2$  from (147) and (148), using expressions (168) and (169) for  $\mathbf{G}_0$  and  $(\omega \mathbf{I} - \mathbf{H})$ . The abbreviation

$$N \equiv \omega^2 - (\sqrt{h^2 + |D|^2} - i\eta)^2 \quad (170)$$

will be employed for the denominator of  $\mathbf{G}_0$  in (168), and the limit  $\eta \rightarrow 0^+$ , to be taken at the end of the calculation, is implied everywhere.

## 5.6 Results up to second order in $\hbar$

The method described in the preceding sections allows us to determine  $\mathcal{G}(\mathbf{R}, \mathbf{p}, \omega)$  and  $\mathcal{F}(\mathbf{R}, \mathbf{p}, \omega)$  up to second order in  $\hbar$  (and, in principle, to any higher order). The required calculations are quite lengthy but without fundamental difficulties, and in the following we shall only summarize the results. We introduce the following notations:

$$[\widehat{XY}] \equiv \nabla_R X \cdot \nabla_p Y - \nabla_p X \cdot \nabla_R Y \quad (171)$$

$$\widehat{(XY)} \equiv \sum_{i,k=1}^3 \left( \partial_{R_i R_k}^2 X \partial_{p_i p_k}^2 Y + \partial_{p_i p_k}^2 X \partial_{R_i R_k}^2 Y - 2\partial_{R_i p_k}^2 X \partial_{p_i R_k}^2 Y \right) \quad (172)$$

$$\widehat{(XYZ)} \equiv \sum_{i,k=1}^3 \left( \partial_{R_i R_k}^2 X \partial_{p_i} Y \partial_{p_k} Z + \partial_{p_i p_k}^2 X \partial_{R_i} Y \partial_{R_k} Z - \partial_{R_i p_k}^2 X \partial_{p_i} Y \partial_{R_k} Z - \partial_{R_i p_k}^2 X \partial_{R_k} Y \partial_{p_i} Z \right), \quad (173)$$

where  $X$ ,  $Y$  or  $Z$  can stand for  $h$ ,  $D$  or  $D^*$ , respectively. In zero order we then have:

$$\mathcal{G}_0(\mathbf{R}, \mathbf{p}, \omega) = \frac{\omega + h}{N} \quad (174)$$

$$\mathcal{F}_0(\mathbf{R}, \mathbf{p}, \omega) = \frac{D}{N} \quad (175)$$

First order:

$$\mathcal{G}_1(\mathbf{R}, \mathbf{p}, \omega) = \frac{i}{2N^2} \left\{ (\omega + h)[\widehat{D^* D}] + D^*[\widehat{D h}] - D[\widehat{D^* h}] \right\} \quad (176)$$

$$\mathcal{F}_1(\mathbf{R}, \mathbf{p}, \omega) = \frac{i\omega}{N^2} [\widehat{Dh}] \quad (177)$$

Second order:

$$\begin{aligned} \mathcal{G}_2(\mathbf{R}, \mathbf{p}, \omega) &= \frac{1}{2N^4} \left\{ |D|^2 (\omega + h) [\widehat{DD^*}]^2 \right. \\ &\quad - (\omega + h) \left[ D^{*2} [\widehat{Dh}]^2 + D^2 [\widehat{D^*h}]^2 \right] \\ &\quad + \left[ (\omega + h)^2 - |D|^2 \right] \left[ D^* [\widehat{DD^*}] [\widehat{Dh}] + D [\widehat{D^*D}] [\widehat{D^*h}] \right] \\ &\quad \left. - 2 \left[ |D|^2 (\omega - h) + 2\omega h (\omega + h) \right] [\widehat{Dh}] [\widehat{D^*h}] \right\} \\ &- \frac{1}{8N^3} \left\{ \left[ (\omega + h)^3 - (\omega + 3h) |D|^2 \right] (\widehat{hh}) \right. \\ &\quad + (\omega^2 + 4\omega h + 3h^2 - |D|^2) \left[ D^* (\widehat{hD}) + D (\widehat{hD^*}) \right] \\ &\quad + (\omega + h) (\omega^2 - h^2 + |D|^2) (\widehat{DD^*}) \\ &\quad \left. + (\omega + h) \left[ D^{*2} (\widehat{DD}) + D^2 (\widehat{D^*D^*}) \right] \right\} \\ &- \frac{1}{4N^4} \left\{ \left[ (\omega + h)^4 - (2\omega^2 + 4\omega h + 6h^2 - |D|^2) |D|^2 \right] (\widehat{hhh}) \right. \\ &\quad + 4h \left[ (\omega + h)^2 - |D|^2 \right] \left[ D (\widehat{hhD^*}) + D^* (\widehat{hhD}) \right] \\ &\quad + \left[ (\omega^2 - h^2) (3\omega^2 + 4\omega h + h^2 - 4|D|^2) + |D|^4 \right] (\widehat{hDD^*}) \\ &\quad + \left[ (\omega + h)^2 - |D|^2 \right] \left[ D^2 (\widehat{hD^*D^*}) + D^{*2} (\widehat{hDD}) \right] \\ &\quad + 2(\omega + h) (\omega^2 + h^2 - |D|^2) \left[ D^* (\widehat{Dhh}) + D (\widehat{D^*hh}) \right] \\ &\quad - \left[ (\omega^2 - h^2)^2 - 2(\omega + h)^2 |D|^2 + |D|^4 \right] \left[ (\widehat{DhD^*}) + (\widehat{D^*hD}) \right] \\ &\quad + 4h(\omega + h) \left[ D^2 (\widehat{D^*hD^*}) + D^{*2} (\widehat{DhD}) \right] \\ &\quad + 2(\omega + h) (\omega^2 - h^2) \left[ D^* (\widehat{DDD^*}) + D (\widehat{D^*DD^*}) \right] \\ &\quad + |D|^2 (\omega + h) \left[ D (\widehat{DD^*D^*}) + D^* (\widehat{D^*DD}) \right] \\ &\quad \left. + (\omega + h) \left[ D^3 (\widehat{D^*D^*D^*}) + D^{*3} (\widehat{DDD}) \right] \right\} \quad (178) \end{aligned}$$

$$\begin{aligned} \mathcal{F}_2(\mathbf{R}, \mathbf{p}, \omega) &= \frac{1}{2N^4} \left\{ D (\omega^2 - h^2) [\widehat{DD^*}]^2 \right. \\ &\quad - D^* (2\omega^2 - 2h^2 - |D|^2) [\widehat{Dh}]^2 - D^3 [\widehat{D^*h}]^2 \\ &\quad + 2h (\omega^2 - h^2) [\widehat{DD^*}] [\widehat{Dh}] + 2h D^2 [\widehat{D^*D}] [\widehat{D^*h}] \\ &\quad \left. - 2D (\omega^2 + h^2) [\widehat{Dh}] [\widehat{D^*h}] \right\} \\ &- \frac{1}{8N^3} \left\{ D (\omega^2 + 3h^2 - |D|^2) (\widehat{hh}) \right. \\ &\quad + 4h D^2 (\widehat{hD^*}) + 2h (\omega^2 - h^2 + |D|^2) (\widehat{hD}) \\ &\quad \left. + 2D (\omega^2 - h^2) (\widehat{DD^*}) \right\} \end{aligned}$$



$$\begin{aligned}
& + D^*(\omega^2 - h^2)(\overline{DD}) + D^3(\overline{D^*D^*}) \} \\
- \frac{1}{4N^4} & \left\{ 4hD(\omega^2 + h^2 - |D|^2)(\overline{hhh}) \right. \\
& + 8h^2D^2(\overline{hhD^*}) - 2[(\omega^2 - h^2)^2 - 2|D|^2(\omega^2 + h^2) + |D|^4](\overline{hhD}) \\
& + 4hD(\omega^2 - h^2)(\overline{hDD^*}) \\
& + 2hD^3(\overline{hD^*D^*}) + 2hD^*|D|^2(\overline{hDD}) \\
& + [(\omega^2 - h^2)(3\omega^2 + h^2) + |D|^2(|D|^2 - 4\omega^2 + 4h^2)](\overline{Dhh}) \\
& + 2D^2(\omega^2 + h^2 - |D|^2)(\overline{D^*hh}) \\
& + 4hD(\omega^2 - h^2)(\overline{DhD^*}) + 4hD|D|^2(\overline{D^*hD}) \\
& + 4hD^3(\overline{D^*hD^*}) + 4hD^*(\omega^2 - h^2)(\overline{DhD}) \\
& + 2(\omega^2 - h^2)^2(\overline{DDD^*}) + 2D^2(\omega^2 - h^2)(\overline{D^*DD^*}) \\
& + D^2(\omega^2 - h^2)(\overline{DD^*D^*}) - (\omega^2 - h^2)(\omega^2 - h^2 - 2|D|^2)(\overline{D^*DD}) \\
& \left. + D^4(\overline{D^*D^*D^*}) + D^{*2}(\omega^2 - h^2)(\overline{DDD}) \right\} \tag{179}
\end{aligned}$$

The results for  $\mathcal{G}$  and  $\mathcal{F}$  can now be inserted into (156) and (157), separately for each order. Because  $\epsilon > 0$  we have to close the path of the integration in (156) in the upper half of the complex  $\omega$  plane; in (157), on the other hand, we have  $\epsilon < 0$  and consequently take the lower half of the complex  $\omega$  plane to complete the semicircle. We write

$$\gamma_n(\mathbf{R}, \mathbf{p}) = -\frac{i}{2\pi} \lim_{\substack{\eta \rightarrow 0^+ \\ \epsilon \rightarrow 0^+}} \oint d\omega e^{i\omega\epsilon} \mathcal{G}_n(\mathbf{R}, \mathbf{p}, \omega) \tag{180}$$

$$\Delta_n(\mathbf{R}, \mathbf{p}) = \frac{i}{2\pi} \lim_{\substack{\eta \rightarrow 0^+ \\ \epsilon \rightarrow 0^-}} \oint d\omega e^{i\omega\epsilon} \mathcal{F}_n(\mathbf{R}, \mathbf{p}, \omega) \ . \tag{181}$$

If we now take into account the additional minus sign in (181) coming from the mathematically negative orientation of the path of integration, we can express the results in terms of residues:

$$\gamma_n(\mathbf{R}, \mathbf{p}) = \lim_{\eta \rightarrow 0^+} \text{Res}[\mathcal{G}_n(\mathbf{R}, \mathbf{p}, \omega) ; \omega = -\sqrt{h^2 + |D|^2} + i\eta] \tag{182}$$

$$\Delta_n(\mathbf{R}, \mathbf{p}) = \lim_{\eta \rightarrow 0^+} \text{Res}[\mathcal{F}_n(\mathbf{R}, \mathbf{p}, \omega) ; \omega = \sqrt{h^2 + |D|^2} - i\eta] \ . \tag{183}$$

The calculation of the residues can be performed in a straightforward way with the usual methods of complex analysis; again, we shall give only the results. Zero order:

$$\gamma_0(\mathbf{R}, \mathbf{p}) = \frac{1}{2} \left( 1 - \frac{h}{\sqrt{h^2 + |D|^2}} \right) \tag{184}$$

$$\Delta_0(\mathbf{R}, \mathbf{p}) = \frac{1}{2} \frac{D}{\sqrt{h^2 + |D|^2}} \quad (185)$$

First order:

$$\gamma_1(\mathbf{R}, \mathbf{p}) = \frac{i}{8(h^2 + |D|^2)^{\frac{3}{2}}} \left\{ h[\widehat{D^*D}] + D^*[\widehat{Dh}] - D[\widehat{D^*h}] \right\} \quad (186)$$

$$\Delta_1(\mathbf{R}, \mathbf{p}) = 0 \quad (187)$$

Second order:

$$\begin{aligned} \gamma_2(\mathbf{R}, \mathbf{p}) = & \frac{1}{64(h^2 + |D|^2)^{\frac{7}{2}}} \left\{ 5h|D|^2[\widehat{DD^*}]^2 \right. \\ & - 5h \left[ D^{*2}[\widehat{Dh}]^2 + D^2[\widehat{D^*h}]^2 \right] \\ & + 2(2h^2 - 3|D|^2) \left[ D^*[\widehat{DD^*}][\widehat{Dh}] + D[\widehat{D^*D}][\widehat{D^*h}] \right] \\ & \left. + 2h(2h^2 + 7|D|^2)[\widehat{Dh}][\widehat{D^*h}] \right\} \\ - & \frac{1}{128(h^2 + |D|^2)^{\frac{5}{2}}} \left\{ 12h|D|^2(\widehat{hh}) \right. \\ & - 4(2h^2 - |D|^2) \left[ D^*(\widehat{hD}) + D(\widehat{hD^*}) \right] \\ & + 2h(2h^2 - |D|^2)(\widehat{DD^*}) \\ & \left. - 3h \left[ D^{*2}(\widehat{DD}) + D^2(\widehat{D^*D^*}) \right] \right\} \\ - & \frac{1}{128(h^2 + |D|^2)^{\frac{7}{2}}} \left\{ 8|D|^2(|D|^2 - 4h^2)(\widehat{hhh}) \right. \\ & + 8h(2h^2 - 3|D|^2) \left[ D(\widehat{hhD^*}) + D^*(\widehat{hhD}) \right] \\ & + 4|D|^2(8h^2 + 3|D|^2)(\widehat{hDD^*}) \\ & + 2(2h^2 - 3|D|^2) \left[ D^2(\widehat{hD^*D^*}) + D^{*2}(\widehat{hDD}) \right] \\ & + 4h(2h^2 - 3|D|^2) \left[ D^*(\widehat{Dhh}) + D(\widehat{D^*hh}) \right] \\ & - 4(2h^4 - h^2|D|^2 + 2|D|^4) \left[ (\widehat{DhD^*}) + (\widehat{D^*hD}) \right] \\ & + 20h^2 \left[ D^2(\widehat{D^*hD^*}) + D^{*2}(\widehat{DhD}) \right] \\ & - 2h(6h^2 + |D|^2) \left[ D^*(\widehat{DDD^*}) + D(\widehat{D^*DD^*}) \right] \\ & + 5h|D|^2 \left[ D(\widehat{DD^*D^*}) + D^*(\widehat{D^*DD}) \right] \\ & \left. + 5h \left[ D^3(\widehat{D^*D^*D^*}) + D^{*3}(\widehat{DDD}) \right] \right\} \quad (188) \end{aligned}$$

$$\begin{aligned} \Delta_2(\mathbf{R}, \mathbf{p}) = & \frac{1}{64(h^2 + |D|^2)^{\frac{7}{2}}} \left\{ D(6h^2 + |D|^2)[\widehat{DD^*}]^2 \right. \\ & - D^*(12h^2 + 7D^2)[\widehat{Dh}]^2 + 5D^3[\widehat{D^*h}]^2 \\ & + 2h(6h^2 + |D|^2)[\widehat{DD^*}][\widehat{Dh}] - 10hD^2[\widehat{D^*D}][\widehat{D^*h}] \\ & \left. + 2D(4h^2 - |D|^2)[\widehat{Dh}][\widehat{D^*h}] \right\} \end{aligned}$$

$$\begin{aligned}
& - \frac{1}{128(h^2 + |D|^2)^{\frac{5}{2}}} \left\{ 4D(2h^2 - |D|^2) \overbrace{(hh)} + \right. \\
& \quad + 12hD^2 \overbrace{(hD^*)} - 4h(2h^2 - |D|^2) \overbrace{(hD)} \\
& \quad - 2D(4h^2 + |D|^2) \overbrace{(DD^*)} \\
& \quad \left. - D^*(4h^2 + |D|^2) \overbrace{(DD)} + 3D^3 \overbrace{(D^*D^*)} \right\} \\
& + \frac{1}{128(h^2 + |D|^2)^{\frac{7}{2}}} \left\{ 8hD(2h^2 - 3|D|^2) \overbrace{(hhh)} \right. \\
& \quad + 40h^2D^2 \overbrace{(hhD^*)} - 8(2h^4 - h^2|D|^2 + 2|D|^4) \overbrace{(hhD)} \\
& \quad - 4hD(6h^2 + |D|^2) \overbrace{(hDD^*)} \\
& \quad + 10hD^3 \overbrace{(hD^*D^*)} + 10hD^*|D|^2 \overbrace{(hDD)} \\
& \quad + 4|D|^2(8h^2 + 3|D|^2) \overbrace{(Dhh)} + 4D^2(2h^2 - 3|D|^2) \overbrace{(D^*hh)} \\
& \quad - 4hD(6h^2 + |D|^2) \overbrace{(DhD^*)} + 20hD|D|^2 \overbrace{(D^*hD)} \\
& \quad + 20hD^3 \overbrace{(D^*hD^*)} - 4hD^*(6h^2 + |D|^2) \overbrace{(DhD)} \\
& \quad + 2(8h^4 + 4h^2|D|^2 + |D|^4) \overbrace{(DDD^*)} - 2D^2(6h^2 + |D|^2) \overbrace{(D^*DD^*)} \\
& \quad - D^2(6h^2 + |D|^2) \overbrace{(DD^*D^*)} - (8h^4 + 16h^2|D|^2 + 3|D|^4) \overbrace{(D^*DD)} \\
& \quad \left. + 5D^4 \overbrace{(D^*D^*D^*)} - D^{*2}(6h^2 + |D|^2) \overbrace{(DDD)} \right\} \quad (189)
\end{aligned}$$

## 5.7 Discussion of the results

Let us first consider the result for the zero-order normal density,

$$n_0(\mathbf{R}) = \int \frac{d^3p}{(2\pi\hbar)^3} \left( 1 - \frac{h}{\sqrt{h^2 + |D|^2}} \right), \quad (190)$$

which originates from insertion of (184) into (149), and the anomalous density (185). Both densities can also be derived from the results for the homogeneous non-interacting “bogoliubon” gas (Dreizler and Gross 1990) if  $\mu$  and  $D_s(\mathbf{p})$  are replaced by  $\mu(\mathbf{R})$  and  $D_s(\mathbf{R}, \mathbf{p})$ . This procedure constitutes the superconducting analogue of the LDA discussed in section 3.1.

Furthermore, from Eqs. (186) and (187) we see that *both* the normal and anomalous first-order densities,  $n_1(\mathbf{R})$  and  $\Delta_1(\mathbf{R}, \mathbf{p})$ , *vanish identically*. The reason for  $n_1(\mathbf{R}) = 0$  is that  $\gamma_1(\mathbf{R}, \mathbf{p})$  is an *odd* function of  $\mathbf{p}$ . This, on the other hand, follows from the fact that both  $h$  and  $D$  [see Eqs. (138) and (128)] are *even* functions of  $\mathbf{p}$ , and therefore their gradient with respect to  $\mathbf{p}$  is odd.

The second-order density matrix  $\gamma_2(\mathbf{R}, \mathbf{p})$  is again an even function of  $\mathbf{p}$  so that, in general, all of the terms in Eq. (188) will also appear in the second-order density  $n_2(\mathbf{R})$ .

Next we want to investigate if the results section 5.6 reduce to the well-known normal-state electron gas results in the limit  $D \rightarrow 0$ . It is clear that in this limit the anomalous

Green's function as well as the anomalous density must vanish.

We start by assuming  $D_s(\mathbf{r}, \mathbf{r}') \equiv 0$  in the Hamiltonian (88); the semiclassical expansion then becomes much easier to perform, as there are no more contributions containing odd powers of  $\hbar$  (Grammaticos and Voros 1979). We find, designating the normal state by “ $NS$ ”:

$$\mathcal{G}_0^{NS}(\mathbf{R}, \mathbf{p}, \omega) = \frac{1}{\omega - h + i\eta \text{sign}(h)} \quad (191)$$

$$\begin{aligned} \mathcal{G}_2^{NS}(\mathbf{R}, \mathbf{p}, \omega) = & -\frac{1}{4} \sum_{i,k=1}^3 \left\{ \frac{\partial_{R_i R_k}^2 h \partial_{p_i p_k}^2 h}{(\omega - h + i\eta \text{sign}(h))^3} \right. \\ & \left. + \frac{\partial_{R_i R_k}^2 h \partial_{p_i} h \partial_{p_k} h + \partial_{p_i p_k}^2 h \partial_{R_i} h \partial_{R_k} h}{(\omega - h + i\eta \text{sign}(h))^4} \right\} . \end{aligned} \quad (192)$$

The integration (180) over  $\omega$  directly leads to the normal-state density matrix (52), where we have to use the following formula for the second-order terms:

$$\lim_{\eta \rightarrow 0^+} \oint \frac{d\omega}{2\pi i} \frac{e^{i\omega 0^+}}{(\omega - h + i\eta \text{sign}(h))^n} = -\frac{1}{(n-1)!} \left( \frac{d}{dh} \right)^{n-2} \delta(h) \quad (193)$$

for  $n \geq 2$ . The explicit result (Grammaticos and Voros 1979) is given up to second order by

$$\begin{aligned} \gamma^{NS}(\mathbf{R}, \mathbf{p}) = & \theta(-h) + \frac{\hbar^2}{8} \sum_{i,k=1}^3 \partial_{R_i R_k}^2 h \partial_{p_i p_k}^2 h \delta'(h) \\ & + \frac{\hbar^2}{24} \sum_{i,k=1}^3 (\partial_{R_i R_k}^2 h \partial_{p_i} h \partial_{p_k} h + \partial_{p_i p_k}^2 h \partial_{R_i} h \partial_{R_k} h) \delta''(h) . \end{aligned} \quad (194)$$

The normal-state particle and kinetic energy densities are then obtained by inserting the density matrix (194) into Eqs. (149) and (150), respectively:

$$n[\mu](\mathbf{R}) = \frac{(2m)^{\frac{3}{2}}}{3\pi^2 \hbar^3} \mu(\mathbf{R})^{\frac{3}{2}} + \hbar^2 \frac{\sqrt{2m}}{24\pi^2 \hbar^3} \frac{\nabla^2 \mu(\mathbf{R})}{\sqrt{\mu(\mathbf{R})}} - \hbar^2 \frac{\sqrt{2m}}{96\pi^2 \hbar^3} \frac{(\nabla \mu(\mathbf{R}))^2}{\mu(\mathbf{R})^{\frac{3}{2}}} \quad (195)$$

$$\begin{aligned} t_s[\mu](\mathbf{R}) = & \frac{\hbar^2}{2m} \frac{\nabla^2}{4} n[\mu](\mathbf{R}) \\ & + \frac{(2m)^{\frac{3}{2}}}{5\pi^2 \hbar^3} \mu(\mathbf{R})^{\frac{5}{2}} + \hbar^2 \frac{\sqrt{2m}}{12\pi^2 \hbar^3} \sqrt{\mu(\mathbf{R})} \nabla^2 \mu(\mathbf{R}) + \hbar^2 \frac{\sqrt{2m}}{32\pi^2 \hbar^3} \frac{(\nabla \mu(\mathbf{R}))^2}{\sqrt{\mu(\mathbf{R})}} . \end{aligned} \quad (196)$$

We now demonstrate that the above results can also be found by letting  $D \rightarrow 0$  in the expressions (174)–(179) and (184)–(189) for the superconducting case. This is easily verified for the Green's functions. The denominator (170) becomes

$$N \xrightarrow{D \rightarrow 0} \omega^2 - (|h| - i\eta)^2 , \quad (197)$$

and only those numerators survive which do not explicitly contain  $D$  or its derivatives. This directly leads from (174) to (191) and from (178) to (192).

Things are more complicated for the density matrix. For the zero-order term, it is straightforward to see that

$$\gamma_0(\mathbf{R}, \mathbf{p}) = \frac{1}{2} \left( 1 - \frac{h}{\sqrt{h^2 + |D|^2}} \right) \xrightarrow{D \rightarrow 0} \theta(-h) = \gamma_0^{NS}(\mathbf{R}, \mathbf{p}) \quad , \quad (198)$$

but in second order it seems at first sight that all terms vanish if one sets  $D \equiv 0$  in (188). Indeed this will always happen except for  $h = 0$ . Because  $\gamma(\mathbf{R}, \mathbf{p})$  appears under an integral over  $p$  in (149) and (150), it is necessary to understand the limit  $D \rightarrow 0$  in a distributional sense. Starting from (198) and differentiating repeatedly with respect to  $h$  on both sides, we can generate the following series of relations:

$$\frac{1}{2} \left( 1 - \frac{h}{\sqrt{h^2 + |D|^2}} \right) \xrightarrow{D \rightarrow 0} \theta(-h) \quad (199)$$

$$-\frac{1}{2} \frac{|D|^2}{(h^2 + |D|^2)^{\frac{3}{2}}} \xrightarrow{D \rightarrow 0} -\delta(h) \quad (200)$$

$$\frac{3}{2} \frac{h|D|^2}{(h^2 + |D|^2)^{\frac{5}{2}}} \xrightarrow{D \rightarrow 0} -\delta'(h) \quad (201)$$

$$\frac{3}{2} \frac{|D|^2(|D|^2 - 4h^2)}{(h^2 + |D|^2)^{\frac{7}{2}}} \xrightarrow{D \rightarrow 0} -\delta''(h) \quad . \quad (202)$$

It is easily verified that the left-hand sides of (200)–(202) are indeed representations of the Dirac  $\delta$ -function and its derivatives: if one calculates the integral over  $h$  together with a test function  $f(h)$  that can be expanded in a Taylor series around  $h = 0$ , one finds, e. g., for (200):

$$-\frac{1}{2} \lim_{D \rightarrow 0} \int dh \frac{|D|^2}{(h^2 + |D|^2)^{\frac{3}{2}}} f(h) = -f(0) \quad . \quad (203)$$

The other two relations are verified analogously. If we now closely examine Eq. (188), we find that we can use (201) and (202) to recover  $\gamma_2^{NS}(\mathbf{R}, \mathbf{p})$  as given in expression (194):

$$\begin{aligned} & -\frac{1}{64(h^2 + |D|^2)^{\frac{5}{2}}} \sum_{i,k=1}^3 12h|D|^2 \partial_{R_i R_k}^2 h \partial_{p_i p_k}^2 h \\ & -\frac{1}{128(h^2 + |D|^2)^{\frac{7}{2}}} \sum_{i,k=1}^3 8|D|^2(|D|^2 - 4h^2) (\partial_{R_i R_k}^2 h \partial_{p_i} h \partial_{p_k} h + \partial_{p_i p_k}^2 h \partial_{R_i} h \partial_{R_k} h) \\ & \xrightarrow{D \rightarrow 0} \frac{1}{8} \sum_{i,k=1}^3 \partial_{R_i R_k}^2 h \partial_{p_i p_k}^2 h \delta'(h) + \frac{1}{24} \sum_{i,k=1}^3 (\partial_{R_i R_k}^2 h \partial_{p_i} h \partial_{p_k} h + \partial_{p_i p_k}^2 h \partial_{R_i} h \partial_{R_k} h) \delta''(h) \\ & = \gamma_2^{NS}(\mathbf{R}, \mathbf{p}) \quad . \end{aligned} \quad (204)$$

Thus, our expression for the superconducting density matrix gives the correct non-superconducting limit.

## 6 Density-gradient expansion for superconductors

### 6.1 Preliminaries

In section 3.2 we presented the principles of gradient expansion for normal-state systems. Now our aim is to apply this technique to superconductors. The first step has already been made in section 5, where we performed a semiclassical expansion of the density matrix  $\gamma$  and the anomalous density  $\Delta$ , Eqs. (158) and (159), with the results for  $\gamma_n$  and  $\Delta_n$  given by Eqs. (184)–(189). We note that in these expansions the powers of  $\hbar$  (i. e., the indices  $n$ ) correspond to the orders of derivatives with respect to  $\mathbf{R}$  and  $\mathbf{p}$  of  $h$  and  $D$ . In analogy to Eq. (52) we have:

$$\gamma(\mathbf{R}, \mathbf{p}) = \gamma[\mu, D, \partial_i \mu, \partial_i D, \partial_i \partial_k \mu, \partial_i \partial_k D, \dots](\mathbf{R}, \mathbf{p}) \quad (205)$$

$$\Delta(\mathbf{R}, \mathbf{p}) = \Delta[\mu, D, \partial_i \mu, \partial_i D, \partial_i \partial_k \mu, \partial_i \partial_k D, \dots](\mathbf{R}, \mathbf{p}) \quad . \quad (206)$$

It is obvious that, in contrast to the normal-state case described in 3.2,  $\gamma$  and  $\Delta$  now have a twofold functional dependence, on  $\mu(\mathbf{R})$  and  $D(\mathbf{R}, \mathbf{p})$ , and we must find a way to eliminate *both* quantities to obtain the density functional  $T_s[n, \Delta]$ . Consequently, the next step has to be the inversion of the functionals  $n[\mu, D]$  and  $\Delta[\mu, D]$  to determine the density functionals

$$\mu(\mathbf{R}) = \mu[n, \Delta, \partial_i n, \partial_i \Delta, \partial_i \partial_k n, \partial_i \partial_k \Delta \dots](\mathbf{R}) \quad (207)$$

$$D(\mathbf{R}, \mathbf{p}) = D[n, \Delta, \partial_i n, \partial_i \Delta, \partial_i \partial_k n, \partial_i \partial_k \Delta \dots](\mathbf{R}, \mathbf{p}) \quad (208)$$

and insertion of these functionals into the expression (150) for the kinetic energy density  $t_s[\mu, D]$ . During the whole procedure we have to watch for consistency up to second order in the derivatives.

Obviously, the contribution  $\frac{\hbar^2}{2m} \frac{\nabla^2}{4} n(\mathbf{R})$  to the kinetic energy density (150) is a density functional already, so it does not take part in the elimination process indicated above. We therefore write the kinetic energy density as

$$t_s[\mu, D] = \frac{\hbar^2}{2m} \frac{\nabla^2}{4} n(\mathbf{R}) + \tau[\mu, D] \quad (209)$$

where

$$\tau[\mu, D](\mathbf{R}) = 2 \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} \gamma[\mu, D](\mathbf{R}, \mathbf{p}) \quad . \quad (210)$$

We now want to execute a few preliminary calculations and consider only the zero-order densities:

$$n_0[\mu, D](\mathbf{R}) = \int \frac{d^3 p}{(2\pi\hbar)^3} \left( 1 - \frac{h}{\sqrt{h^2 + |D|^2}} \right) \quad (211)$$

$$\Delta_0[\mu, D](\mathbf{R}, \mathbf{p}) = \frac{1}{2} \frac{D}{\sqrt{\hbar^2 + |D|^2}} \quad . \quad (212)$$

There is no difficulty in solving Eq. (212) for  $D$ :

$$D[\mu, \Delta_0] = \frac{2\Delta_0|h|}{\sqrt{1 - 4|\Delta_0|^2}} \quad . \quad (213)$$

Insertion into (211) results in

$$n_0[\mu, \Delta_0](\mathbf{R}) = \int \frac{d^3p}{(2\pi\hbar)^3} \left( 1 - \text{sign}(h) \sqrt{1 - 4|\Delta_0(\mathbf{R}, \mathbf{p})|^2} \right) \quad (214)$$

where  $h = \frac{p^2}{2m} - \mu(\mathbf{R})$ . Obviously, Eq. (214) cannot be solved analytically for  $\mu(\mathbf{R})$ . We emphasize, however, that the right-hand side of Eq. (214) is a simple *function* of  $\mu$  which can easily be tabulated and inverted numerically. In the following, the inverse function is assumed to be known and we write

$$\mu[n_0, \Delta_0](\mathbf{R}) = \left( \int \frac{d^3p}{(2\pi\hbar)^3} \left( 1 - \text{sign}(h) \sqrt{1 - 4|\Delta_0|^2} \right) \right)^{-1} \quad . \quad (215)$$

If all higher orders are neglected,  $n_0$  and  $\Delta_0$  can be replaced by  $n$  and  $\Delta$ . This leads to the final result for the zero-order kinetic energy:

$$T_s^{(0)}[n, \Delta] = \int d^3R \int \frac{d^3p}{(2\pi\hbar)^3} \frac{p^2}{2m} \left( 1 - \text{sign} \left( \frac{p^2}{2m} - \mu[n, \Delta] \right) \sqrt{1 - 4|\Delta|^2} \right) \quad . \quad (216)$$

In the next section we present the method how to obtain the functional  $T_s[n, \Delta]$  up to second order. Explicit results will be given in 6.3. Finally, in section 6.4 we shall discuss the normal-state limit.

## 6.2 Method for the inversion

Starting point of the inversion procedure are the normal and anomalous densities,

$$n(\mathbf{R}) = n_0[\mu, D](\mathbf{R}) + \hbar^2 n_2[\mu, D](\mathbf{R}) + \dots \quad (217)$$

$$\Delta(\mathbf{R}, \mathbf{p}) = \Delta_0[\mu, D](\mathbf{R}, \mathbf{p}) + \hbar^2 \Delta_2[\mu, D](\mathbf{R}, \mathbf{p}) + \dots \quad (218)$$

In order to execute the next step of the gradient expansion procedure, we now have to invert the functionals (217) and (218) and establish the expansions

$$\mu[n, \Delta](\mathbf{R}) = \mu_0[n, \Delta](\mathbf{R}) + \mu_1[n, \Delta](\mathbf{R}) + \mu_2[n, \Delta](\mathbf{R}) + \dots \quad (219)$$

$$D[n, \Delta](\mathbf{R}, \mathbf{p}) = D_0[n, \Delta](\mathbf{R}, \mathbf{p}) + D_1[n, \Delta](\mathbf{R}, \mathbf{p}) + D_2[n, \Delta](\mathbf{R}, \mathbf{p}) + \dots \quad (220)$$

where the indices again denote orders in the derivatives.

To explicitly derive the unknown functionals in (219) and (220) we start with the zero-order results from section 6.1. From Eq. (213) we have

$$D[n_0, \Delta_0](\mathbf{R}, \mathbf{p}) = \frac{2\Delta_0}{\sqrt{1 - 4|\Delta_0|^2}} \left| \frac{p^2}{2m} - \mu[n_0, \Delta_0](\mathbf{R}) \right| \quad , \quad (221)$$

and  $\mu[n_0, \Delta_0]$  is given by Eq. (215).

The crucial idea is to rewrite the zero-order densities in (215) and (221) as

$$n_0(\mathbf{R}) = n(\mathbf{R}) - \hbar^2 n_2(\mathbf{R}) \quad (222)$$

$$\Delta_0(\mathbf{R}, \mathbf{p}) = \Delta(\mathbf{R}, \mathbf{p}) - \hbar^2 \Delta_2(\mathbf{R}, \mathbf{p}) \quad (223)$$

which is correct up to the second order in  $\hbar$ . This is because  $n(\mathbf{R})$  and  $\Delta(\mathbf{R}, \mathbf{p})$  are the exact densities given by Eqs. (217) and (218), i. e., they contain *all* orders of  $\hbar$  of the semiclassical expansion. If we subtract the second-order contributions  $\hbar^2 n_2$  and  $\hbar^2 \Delta_2$ , then Eqs. (222) and (223) will give the correct zero-order densities plus terms of higher than second order which we do not worry about.

We then make an analogous ansatz for  $\mu_0$  and  $D_0$ :

$$\mu_0[n, \Delta](\mathbf{R}) = \mu[n, \Delta](\mathbf{R}) - \mu_2[n, \Delta](\mathbf{R}) \quad (224)$$

$$D_0[n, \Delta](\mathbf{R}, \mathbf{p}) = D[n, \Delta](\mathbf{R}, \mathbf{p}) - D_2[n, \Delta](\mathbf{R}, \mathbf{p}) \quad . \quad (225)$$

The functionals  $\mu_0[n, \Delta](\mathbf{R})$  and  $D_0[n, \Delta](\mathbf{R}, \mathbf{p})$  are correct up to the second order in the derivatives. They are calculated using Eqs. (222) and (223) in the functionals (215) and (221):

$$\mu_0[n, \Delta](\mathbf{R}) = \mu[n - \hbar^2 n_2, \Delta - \hbar^2 \Delta_2](\mathbf{R}) \quad (226)$$

$$D_0[n, \Delta](\mathbf{R}, \mathbf{p}) = D[n - \hbar^2 n_2, \Delta - \hbar^2 \Delta_2](\mathbf{R}, \mathbf{p}) \quad . \quad (227)$$

To cast Eqs. (226) and (227) in the form (224) and (225), respectively, we have to perform a Taylor expansion for functionals:  $\mu[n_0, \Delta_0]$  and  $D[n_0, \Delta_0]$  have to be expanded about  $n(\mathbf{R})$  and  $\Delta(\mathbf{R}, \mathbf{p})$ . The first two orders of the Taylor expansion of  $\mu_0$  can be written as

$$\begin{aligned} \mu_0(\mathbf{R}) &= \mu[n, \Delta](\mathbf{R}) \\ &+ \int d^3 R' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta n_0(\mathbf{R}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} (n_0(\mathbf{R}') - n(\mathbf{R}')) \\ &+ \int d^3 R' \int d^3 p' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta \Delta_0(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} (\Delta_0(\mathbf{R}', \mathbf{p}') - \Delta(\mathbf{R}', \mathbf{p}')) \\ &+ \int d^3 R' \int d^3 p' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta \Delta_0^*(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} (\Delta_0^*(\mathbf{R}', \mathbf{p}') - \Delta^*(\mathbf{R}', \mathbf{p}')) \quad . \quad (228) \end{aligned}$$

$D_0(\mathbf{R}, \mathbf{p})$  and  $D_0^*(\mathbf{R}, \mathbf{p})$  are expanded analogously. The functional derivatives of  $\mu$  and  $D$  needed in the expansions can be calculated straightforwardly from (215) and (221). For  $\mu[n_0, \Delta_0]$  we use the functional analogue of the well-known rule for the derivative of implicitly defined functions. Results will be given in the next section.



We now insert (222) and (223) and obtain:

$$\begin{aligned}
\mu_0(\mathbf{R}) &= \mu[n, \Delta](\mathbf{R}) \\
&- \int d^3 R' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta n_0(\mathbf{R}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 n_2(\mathbf{R}') \\
&- \int d^3 R' \int d^3 p' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta \Delta_0(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 \Delta_2(\mathbf{R}', \mathbf{p}') \\
&- \int d^3 R' \int d^3 p' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta \Delta_0^*(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 \Delta_2^*(\mathbf{R}', \mathbf{p}') \quad . \quad (229)
\end{aligned}$$

For  $n_2$ ,  $\Delta_2$  and  $\Delta_2^*$  we have to take the functionals

$$n_2[n, \Delta] = n_2[\mu[n, \Delta], D[n, \Delta]] \quad (230)$$

$$\Delta_2[n, \Delta] = \Delta_2[\mu[n, \Delta], D[n, \Delta]] \quad , \quad (231)$$

following from (188) and (189) with (215) and (221). Therefore, upon comparison with Eqs. (224) and (225),

$$\begin{aligned}
\mu_2[n, \Delta](\mathbf{R}) &= \int d^3 R' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta n_0(\mathbf{R}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 n_2[n, \Delta](\mathbf{R}') \\
&+ \int d^3 R' \int d^3 p' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta \Delta_0(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 \Delta_2[n, \Delta](\mathbf{R}', \mathbf{p}') \\
&+ \int d^3 R' \int d^3 p' \frac{\delta \mu[n_0, \Delta_0](\mathbf{R})}{\delta \Delta_0^*(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 \Delta_2^*[n, \Delta](\mathbf{R}', \mathbf{p}') \quad (232)
\end{aligned}$$

and similarly

$$\begin{aligned}
D_2[n, \Delta](\mathbf{R}, \mathbf{p}) &= \int d^3 R' \frac{\delta D[n_0, \Delta_0](\mathbf{R}, \mathbf{p})}{\delta n_0(\mathbf{R}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 n_2[n, \Delta](\mathbf{R}') \\
&+ \int d^3 R' \int d^3 p' \frac{\delta D[n_0, \Delta_0](\mathbf{R}, \mathbf{p})}{\delta \Delta_0(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 \Delta_2[n, \Delta](\mathbf{R}', \mathbf{p}') \\
&+ \int d^3 R' \int d^3 p' \frac{\delta D[n_0, \Delta_0](\mathbf{R}, \mathbf{p})}{\delta \Delta_0^*(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{n_0=n \\ \Delta_0=\Delta}} \hbar^2 \Delta_2^*[n, \Delta](\mathbf{R}', \mathbf{p}') \quad . \quad (233)
\end{aligned}$$

The final step of the gradient expansion procedure now involves insertion of the inverted functionals  $\mu[n, \Delta]$  and  $D[n, \Delta]$  in the kinetic energy density functional (210). We write this functional in the following manner:

$$\tau(\mathbf{R}) = \tau_0[\mu_0, D_0](\mathbf{R}) + \hbar^2 \tau_2[\mu, D](\mathbf{R}) + \dots \quad (234)$$

Here,  $\tau_0$  denotes a zero-order functional in the derivatives; therefore, we have to insert  $\mu_0$  and  $D_0$ . Thus,

$$\tau[n, \Delta](\mathbf{R}) = \tau_0[\mu[n, \Delta] - \mu_2[n, \Delta], D[n, \Delta] - D_2[n, \Delta]](\mathbf{R}) + \hbar^2 \tau_2[\mu[n, \Delta], D[n, \Delta]](\mathbf{R}) \quad . \quad (235)$$

The orders in the derivatives are now separated by again performing a Taylor expansion about  $\mu$  and  $D$ . The final result is given by

$$\begin{aligned}
\tau[n, \Delta](\mathbf{R}) &= \tau_0[\mu[n, \Delta], D[n, \Delta]](\mathbf{R}) \\
&- \int d^3 R' \frac{\delta \tau_0[\mu_0, D_0](\mathbf{R})}{\delta \mu_0(\mathbf{R}')} \Big|_{\substack{\mu_0 = \mu[n, \Delta] \\ D_0 = D[n, \Delta]}} \mu_2[n, \Delta](\mathbf{R}') \\
&- \int d^3 R' \int d^3 p' \frac{\delta \tau_0[\mu_0, D_0](\mathbf{R})}{\delta D_0(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{\mu_0 = \mu[n, \Delta] \\ D_0 = D[n, \Delta]}} D_2[n, \Delta](\mathbf{R}', \mathbf{p}') \\
&- \int d^3 R' \int d^3 p' \frac{\delta \tau_0[\mu_0, D_0](\mathbf{R})}{\delta D_0^*(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{\mu_0 = \mu[n, \Delta] \\ D_0 = D[n, \Delta]}} D_2^*[n, \Delta](\mathbf{R}', \mathbf{p}') \\
&+ \hbar^2 \tau_2[\mu[n, \Delta], D[n, \Delta]](\mathbf{R}) \quad . \quad (236)
\end{aligned}$$

This expression allows us to separate the zero- and second-order contributions, and we define:

$$\tau^{(0)}[n, \Delta](\mathbf{R}) = \tau_0[\mu[n, \Delta], D[n, \Delta]](\mathbf{R}) \quad (237)$$

and

$$\begin{aligned}
\tau^{(2)}[n, \Delta](\mathbf{R}) &= \hbar^2 \tau_2[\mu[n, \Delta], D[n, \Delta]](\mathbf{R}) \\
&- \int d^3 R' \frac{\delta \tau_0[\mu_0, D_0](\mathbf{R})}{\delta \mu_0(\mathbf{R}')} \Big|_{\substack{\mu_0 = \mu[n, \Delta] \\ D_0 = D[n, \Delta]}} \mu_2[n, \Delta](\mathbf{R}') \\
&- \int d^3 R' \int d^3 p' \frac{\delta \tau_0[\mu_0, D_0](\mathbf{R})}{\delta D_0(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{\mu_0 = \mu[n, \Delta] \\ D_0 = D[n, \Delta]}} D_2[n, \Delta](\mathbf{R}', \mathbf{p}') \\
&- \int d^3 R' \int d^3 p' \frac{\delta \tau_0[\mu_0, D_0](\mathbf{R})}{\delta D_0^*(\mathbf{R}', \mathbf{p}')} \Big|_{\substack{\mu_0 = \mu[n, \Delta] \\ D_0 = D[n, \Delta]}} D_2^*[n, \Delta](\mathbf{R}', \mathbf{p}') \quad . \quad (238)
\end{aligned}$$

### 6.3 Results for the kinetic energy functional

In this section we want to derive the explicit result for the kinetic energy density functional (236). The zero-order term  $\tau^{(0)}[n, \Delta](\mathbf{R})$  has already been calculated in 6.1 [see Eq. (216)]. To compute the second-order term (238), we first need the functional derivatives of

$$\tau_0[\mu_0, D_0](\mathbf{R}) = \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} \left( 1 - \frac{\hbar}{\sqrt{\hbar^2 + |D_0|^2}} \right) \quad (239)$$

which are given by

$$\frac{\delta \tau_0[\mu_0, D_0](\mathbf{R})}{\delta \mu_0(\mathbf{R}')} = \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} \frac{|D_0|^2}{(\hbar^2 + |D_0|^2)^{\frac{3}{2}}} \delta(\mathbf{R} - \mathbf{R}') \quad (240)$$

$$\frac{\delta \tau_0[\mu_0, D_0](\mathbf{R})}{\delta D_0(\mathbf{R}', \mathbf{p}')} = \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} \frac{1}{2} \frac{\hbar D_0^*}{(\hbar^2 + |D_0|^2)^{\frac{3}{2}}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{p} - \mathbf{p}') \quad . \quad (241)$$

Insertion of (240), (241) and the complex conjugate of (241) into Eq. (238) yields

$$\tau^{(2)}[n, \Delta](\mathbf{R}) = \hbar^2 \tau_2[\mu[n, \Delta], D[n, \Delta]](\mathbf{R})$$

$$\begin{aligned}
& - \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} \frac{|D|^2}{(h^2 + |D|^2)^{\frac{3}{2}}} \mu_2[n, \Delta](\mathbf{R}) \\
& - \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} \frac{1}{2} \frac{h}{(h^2 + |D|^2)^{\frac{3}{2}}} (D^* D_2[n, \Delta](\mathbf{R}, \mathbf{p}) + D D_2^*[n, \Delta](\mathbf{R}, \mathbf{p})) . \quad (242)
\end{aligned}$$

We now need the functional derivatives of  $\mu[n_0, \Delta_0]$  and  $D[n_0, \Delta_0]$  appearing in (232) and (233). We make the following observation: because of the absolute  $|h|$  and the sign function  $\text{sign}(h)$  contained in (215) and (221), the derivative is not properly defined at  $h = 0$ . Introducing the constant  $a$ , we can deal with this crucial restriction by writing

$$|h| = \lim_{a \rightarrow 0} \sqrt{h^2 + a^2} \quad . \quad (243)$$

We see that  $\sqrt{h^2 + a^2}$  can be differentiated everywhere, and we have instead of (215) and (221):

$$D[n_0, \Delta_0](\mathbf{R}, \mathbf{p}) = \lim_{a \rightarrow 0} 2\Delta_0 \frac{\sqrt{h^2 + a^2}}{\sqrt{1 - 4|\Delta_0|^2}} \quad (244)$$

$$\mu[n_0, \Delta_0](\mathbf{R}) = \lim_{a \rightarrow 0} \left( \int \frac{d^3 p}{(2\pi\hbar)^3} \left( 1 - \frac{h}{\sqrt{h^2 + 4|\Delta_0|^2 a^2}} \sqrt{1 - 4|\Delta_0|^2} \right) \right)^{-1} \quad (245)$$

with  $h = \frac{p^2}{2m} - \mu[n_0, \Delta_0]$ .

At this point we anticipate that the introduction of the constant  $a$  will eventually lead to expressions we have to interpret as distributions. Similarly to section 5.7, we generate a series of relations by repeatedly differentiating with respect to  $h$ :

$$\lim_{a \rightarrow 0} \frac{h}{\sqrt{h^2 + 4|\Delta|^2 a^2}} = \text{sign}(h) \quad (246)$$

$$\lim_{a \rightarrow 0} \frac{1}{2} \frac{4|\Delta|^2 a^2}{(h^2 + 4|\Delta|^2 a^2)^{\frac{3}{2}}} = \delta(h) \quad (247)$$

$$\lim_{a \rightarrow 0} -\frac{3}{2} \frac{4|\Delta|^2 a^2 h}{(h^2 + 4|\Delta|^2 a^2)^{\frac{5}{2}}} = \delta'(h) \quad (248)$$

$$\lim_{a \rightarrow 0} \frac{3}{2} \frac{4|\Delta|^2 a^2 (4h^2 - 4|\Delta|^2 a^2)}{(h^2 + 4|\Delta|^2 a^2)^{\frac{7}{2}}} = \delta''(h) \quad . \quad (249)$$

As usual for distributions appearing under an integral, the limiting process is not to be performed until the integration has been carried out. Also, to simplify notation, the “ $\lim_{a \rightarrow 0}$ ” is implied everywhere.

For the functional derivatives appearing in (232) and (233) we then obtain:

$$\frac{\delta\mu[n_0, \Delta_0](\mathbf{R})}{\delta n_0(\mathbf{R}')} = \frac{\delta(\mathbf{R} - \mathbf{R}')}{\int \frac{d^3 p}{(2\pi\hbar)^3} \frac{4|\Delta_0|^2 a^2}{(h^2 + 4|\Delta_0|^2 a^2)^{\frac{3}{2}}} \sqrt{1 - 4|\Delta_0|^2}} \quad (250)$$

$$\frac{\delta D[n_0, \Delta_0](\mathbf{R}, \mathbf{p})}{\delta n_0(\mathbf{R}')} = - \frac{\delta(\mathbf{R} - \mathbf{R}') \frac{h}{\sqrt{h^2 + a^2}} \frac{2\Delta_0(\mathbf{R}, \mathbf{p})}{\sqrt{1 - 4|\Delta_0|^2}}}{\int \frac{d^3 p}{(2\pi\hbar)^3} \frac{4|\Delta_0|^2 a^2}{(h^2 + 4|\Delta_0|^2 a^2)^{\frac{3}{2}}} \sqrt{1 - 4|\Delta_0|^2}} \quad (251)$$

$$\frac{\delta\mu[n_0, \Delta_0](\mathbf{R})}{\delta\Delta_0(\mathbf{R}', \mathbf{p}')} = - \frac{\int \frac{d^3p}{(2\pi\hbar)^3} \frac{h^2 + a^2}{(h^2 + 4|\Delta_0|^2 a^2)^{\frac{3}{2}}} \frac{2h\Delta_0^*(\mathbf{R}, \mathbf{p})}{\sqrt{1 - 4|\Delta_0|^2}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{p} - \mathbf{p}')}{\int \frac{d^3p}{(2\pi\hbar)^3} \frac{4|\Delta_0|^2 a^2}{(h^2 + 4|\Delta_0|^2 a^2)^{\frac{3}{2}}} \sqrt{1 - 4|\Delta_0|^2}} \quad (252)$$

$$\begin{aligned} \frac{\delta D[n_0, \Delta_0](\mathbf{R}, \mathbf{p})}{\delta\Delta_0(\mathbf{R}', \mathbf{p}')} &= 2\sqrt{h^2 + a^2} \frac{1 - 2|\Delta_0|^2}{(1 - 4|\Delta_0|^2)^{\frac{3}{2}}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{p} - \mathbf{p}') \quad (253) \\ &+ \frac{h}{\sqrt{h^2 + a^2}} \frac{2\Delta_0(\mathbf{R}, \mathbf{p})}{\sqrt{1 - 4|\Delta_0|^2}} \frac{\int \frac{d^3p}{(2\pi\hbar)^3} \frac{h^2 + a^2}{(h^2 + 4|\Delta_0|^2 a^2)^{\frac{3}{2}}} \frac{2h\Delta_0^*(\mathbf{R}, \mathbf{p})}{\sqrt{1 - 4|\Delta_0|^2}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{p} - \mathbf{p}')}{\int \frac{d^3p}{(2\pi\hbar)^3} \frac{4|\Delta_0|^2 a^2}{(h^2 + 4|\Delta_0|^2 a^2)^{\frac{3}{2}}} \sqrt{1 - 4|\Delta_0|^2}} \end{aligned}$$

$$\begin{aligned} \frac{\delta D[n_0, \Delta_0](\mathbf{R}, \mathbf{p})}{\delta\Delta_0^*(\mathbf{R}', \mathbf{p}')} &= \sqrt{h^2 + a^2} \frac{4\Delta_0^2}{(1 - 4|\Delta_0|^2)^{\frac{3}{2}}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{p} - \mathbf{p}') \quad (254) \\ &+ \frac{h}{\sqrt{h^2 + a^2}} \frac{2\Delta_0(\mathbf{R}, \mathbf{p})}{\sqrt{1 - 4|\Delta_0|^2}} \frac{\int \frac{d^3p}{(2\pi\hbar)^3} \frac{h^2 + a^2}{(h^2 + 4|\Delta_0|^2 a^2)^{\frac{3}{2}}} \frac{2h\Delta_0(\mathbf{R}, \mathbf{p})}{\sqrt{1 - 4|\Delta_0|^2}} \delta(\mathbf{R} - \mathbf{R}') \delta(\mathbf{p} - \mathbf{p}')}{\int \frac{d^3p}{(2\pi\hbar)^3} \frac{4|\Delta_0|^2 a^2}{(h^2 + 4|\Delta_0|^2 a^2)^{\frac{3}{2}}} \sqrt{1 - 4|\Delta_0|^2}} \end{aligned}$$

Substituting Eqs. (232) and (233) into Eq. (242) and using Eqs. (244) and (245), we find after a few intermediate steps:

$$\begin{aligned} \tau^{(2)}[n, \Delta](\mathbf{R}) &= 2\hbar^2 \int \frac{d^3p}{(2\pi\hbar)^3} \left( \frac{p^2}{2m} - \frac{\int \frac{d^3p}{(2\pi\hbar)^3} \frac{p^2}{2m} \frac{4|\Delta|^2 a^2}{(h^2 + 4|\Delta|^2 a^2)^{\frac{3}{2}}} \sqrt{1 - 4|\Delta|^2}}{\int \frac{d^3p}{(2\pi\hbar)^3} \frac{4|\Delta|^2 a^2}{(h^2 + 4|\Delta|^2 a^2)^{\frac{3}{2}}} \sqrt{1 - 4|\Delta|^2}} \right) \\ &\left( \gamma_2[n, \Delta](\mathbf{R}, \mathbf{p}) - \frac{h(h^2 + a^2)}{(h^2 + 4|\Delta|^2 a^2)^{\frac{3}{2}}} \frac{(\Delta^* \Delta_2[n, \Delta](\mathbf{R}, \mathbf{p}) + \Delta \Delta_2^*[n, \Delta](\mathbf{R}, \mathbf{p}))}{\sqrt{1 - 4|\Delta|^2}} \right). \quad (255) \end{aligned}$$

To derive an explicit result for  $\tau^{(2)}[n, \Delta](\mathbf{R})$ , the next step consists in calculating  $\gamma_2[n, \Delta]$  and  $\Delta_2[n, \Delta]$ . For this purpose we insert Eq. (244) into (188) and (189), respectively, and use the notations (171)–(173) defined in section 5.6. After a lengthy calculation we obtain:

$$\begin{aligned} \gamma_2[n, \Delta](\mathbf{R}, \mathbf{p}) &= -\frac{\hbar^2}{8} \frac{\sqrt{1 - 4|\Delta|^2}}{(h^2 + 4|\Delta|^2 a^2)^{\frac{7}{2}}} \left\{ 8h|\Delta|^2 \frac{h^2 + a^2}{(1 - 4|\Delta|^2)^3} \left[ h^4(5 - 4|\Delta|^2) \right. \right. \\ &\quad \left. \left. + 2h^2 a^2(1 + 16|\Delta|^2 - 16|\Delta|^4) - a^4(5 - 48|\Delta|^2 + 32|\Delta|^4 + 64|\Delta|^6) \right] [\widehat{\Delta\Delta^*}]^2 \right. \\ &\quad \left. - \frac{4}{(1 - 4|\Delta|^2)^2} \left[ h^6 - h^4 a^2(1 - 16|\Delta|^2) - 2h^2 a^4(1 - 12|\Delta|^2 + 8|\Delta|^4) \right. \right. \\ &\quad \left. \left. + 4|\Delta|^2 a^6(3 - 12|\Delta|^2 + 16|\Delta|^4) \right] [\widehat{\Delta\Delta^*}] [\Delta[\widehat{\Delta^*h}] - \Delta^*[\widehat{\Delta h}]] \right. \\ &\quad \left. + \frac{2}{(1 - 4|\Delta|^2)^2} \frac{ha^2}{(h^2 + a^2)} \left[ 2h^4(1 - 20|\Delta|^2) + h^2 a^2(3 - 56|\Delta|^2 - 80|\Delta|^4) \right. \right. \\ &\quad \left. \left. + a^4(5 - 48|\Delta|^2 - 16|\Delta|^4) \right] [\Delta^* \widehat{[\Delta h]}]^2 + \Delta^2 [\widehat{\Delta^* h}]^2 \right. \\ &\quad \left. - \frac{2}{(1 - 4|\Delta|^2)^2} \frac{ha^2}{(h^2 + a^2)} \left[ 2|\Delta|^2 h^4(8 - 18|\Delta|^2 + 24|\Delta|^4 + 320|\Delta|^6) \right. \right. \end{aligned}$$

$$\begin{aligned}
& + h^2 a^2 (1 + 22|\Delta|^2 - 48|\Delta|^4 + 48|\Delta|^6 + 832|\Delta|^8) \\
& + 2|\Delta|^2 a^4 (7 - 16|\Delta|^2 + 16|\Delta|^4 + 64|\Delta|^6) \left[ \widehat{\Delta h} \widehat{\Delta^* h} \right] \Big\}
\end{aligned}$$

$$\begin{aligned}
& - \frac{\hbar^2}{8} \frac{\sqrt{1-4|\Delta|^2}}{(h^2+4|\Delta|^2 a^2)^{\frac{5}{2}}} \left\{ \frac{|\Delta|^2 a^2 h}{h^2+a^2} \left[ 2h^2 + (3-4|\Delta|^2)a^2 \right] \widehat{hh} \right. \\
& \quad - \frac{1}{1-4|\Delta|^2} \left[ h^4 + 2h^2 a^2 (1-4|\Delta|^2) - 4|\Delta|^2 a^4 \right] \left[ \Delta^* \widehat{h\Delta} + \Delta \widehat{h\Delta^*} \right] \\
& \quad + \frac{h(h^2+a^2)}{(1-4|\Delta|^2)^2} \left[ h^2(1-10|\Delta|^2+8|\Delta|^4) - 2|\Delta|^2 a^2 (1+8|\Delta|^2-16|\Delta|^4) \right] \widehat{\Delta\Delta^*} \\
& \quad \left. - \frac{h(h^2+a^2)}{(1-4|\Delta|^2)^2} \left[ h^2(1+4|\Delta|^2) + a^2(3-8|\Delta|^2+16|\Delta|^4) \right] \left[ \Delta^{*2} \widehat{\Delta\Delta} + \Delta^2 \widehat{\Delta^*\Delta^*} \right] \right\} \\
& + \frac{\hbar^2}{8} \frac{\sqrt{1-4|\Delta|^2}}{(h^2+4|\Delta|^2 a^2)^{\frac{7}{2}}} \left\{ \frac{2|\Delta|^2 a^2}{(h^2+a^2)^2} \left[ 3h^6 + h^4 a^2 (8-12|\Delta|^2) \right. \right. \\
& \quad \left. \left. + h^2 a^4 (4-8|\Delta|^2-16|\Delta|^4) - 4|\Delta|^2 a^6 \right] \widehat{hhh} \right. \\
& \quad - \frac{2}{(1-4|\Delta|^2)} \frac{ha^2}{(h^2+a^2)} \left[ h^4(1-4|\Delta|^2) + 2h^2 a^2 (1-12|\Delta|^2+48|\Delta|^4) \right. \\
& \quad \left. - 4|\Delta|^2 a^4 (3-20|\Delta|^2) \right] \left[ \Delta^* \widehat{hh\Delta} + \Delta \widehat{hh\Delta^*} \right] \\
& \quad + \frac{8|\Delta|^2}{(1-4|\Delta|^2)^2} \left[ h^6(1-2|\Delta|^2) - h^4 a^2 (1-6|\Delta|^2+16|\Delta|^4) \right. \\
& \quad \left. - 4h^2 a^4 (1-5|\Delta|^2+12|\Delta|^4+8|\Delta|^6) - 2|\Delta|^2 a^6 (3-8|\Delta|^2+32|\Delta|^4) \right] \widehat{hh\Delta\Delta^*} \\
& \quad + \frac{4}{(1-4|\Delta|^2)^2} \left[ 2|\Delta|^2 h^6 - 2|\Delta|^2 h^4 a^2 (3-8|\Delta|^2) - h^2 a^4 (1-4|\Delta|^2+48|\Delta|^4-32|\Delta|^6) \right. \\
& \quad \left. + 2|\Delta|^2 a^6 (3-32|\Delta|^2+32|\Delta|^4) \right] \left[ \Delta^{*2} \widehat{hh\Delta\Delta} + \Delta^2 \widehat{hh\Delta^*\Delta^*} \right] \\
& \quad - \frac{1}{(1-4|\Delta|^2)} \frac{ha^2}{(h^2+a^2)} \left[ h^4(3-28|\Delta|^2) + 2h^2 a^2 (1-16|\Delta|^2-16|\Delta|^4) \right. \\
& \quad \left. - 4|\Delta|^2 a^4 (3+4|\Delta|^2) \right] \left[ \Delta^* \widehat{\Delta hh} + \Delta \widehat{\Delta^* hh} \right] \\
& \quad + \frac{2}{(1-4|\Delta|^2)^2} \left[ 2|\Delta|^2 h^6 + h^4 a^2 (1-12|\Delta|^2+56|\Delta|^4) - 2|\Delta|^2 h^2 a^4 (1-8|\Delta|^2-32|\Delta|^4) \right. \\
& \quad \left. + 16|\Delta|^4 a^6 (1-4|\Delta|^2+8|\Delta|^4) \right] \left[ \widehat{\Delta h\Delta^*} + \widehat{\Delta^* h\Delta} \right] \\
& \quad + \frac{4}{(1-4|\Delta|^2)^2} \left[ h^6 - 2h^4 a^2 (1-10|\Delta|^2) - h^2 a^4 (5-40|\Delta|^2+32|\Delta|^4) \right. \\
& \quad \left. + 32|\Delta|^4 a^6 (1-2|\Delta|^2) \right] \left[ \Delta^{*2} \widehat{\Delta h\Delta} + \Delta^2 \widehat{\Delta^* h\Delta^*} \right] \\
& \quad + \frac{4h(h^2+a^2)}{(1-4|\Delta|^2)^3} \left[ h^4(1+4|\Delta|^2) + h^2 a^2 (3-12|\Delta|^2+64|\Delta|^4) \right. \\
& \quad \left. + 2|\Delta|^2 a^4 (1+8|\Delta|^2+16|\Delta|^4) \right] \left[ \Delta^* \widehat{\Delta\Delta\Delta^*} + \Delta \widehat{\Delta^*\Delta\Delta^*} \right] \\
& \quad - \frac{4h(h^2+a^2)}{(1-4|\Delta|^2)^3} \left[ h^4(1-10|\Delta|^2+8|\Delta|^4) + 2|\Delta|^2 a^2 h^2 (3-36|\Delta|^2+32|\Delta|^4) \right. \\
& \quad \left. + a^4 (5|\Delta|^2-32|\Delta|^4-48|\Delta|^6+128|\Delta|^8) \right] \left[ \Delta \widehat{\Delta\Delta^*\Delta^*} + \Delta^* \widehat{\Delta^*\Delta\Delta} \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{4h(h^2 + a^2)}{(1 - 4|\Delta|^2)^3} \left[ 2h^4(1 + 4|\Delta|^2) + 2h^2a^2(1 + 4|\Delta|^2 + 32|\Delta|^4) \right. \\
& \quad \left. - a^4(5 - 48|\Delta|^2 + 80|\Delta|^4 - 128|\Delta|^6) \right] \left[ \Delta^{*3}(\widehat{\Delta\Delta\Delta}) + \Delta^3(\widehat{\Delta^*\Delta^*\Delta^*}) \right] \Big\} \\
& \hspace{15em} (256)
\end{aligned}$$

$$\begin{aligned}
\Delta^* \Delta_2[n, \Delta] + \Delta \Delta_2^*[n, \Delta] &= -\frac{\hbar^2(1 - 4|\Delta|^2)\sqrt{h^2 + a^2}}{8(h^2 + 4|\Delta|^2a^2)^{\frac{7}{2}}} \left\{ 16|\Delta|^2 \frac{h^2 + a^2}{(1 - 4|\Delta|^2)^3} \right. \\
& \quad \left[ h^4(3 - 2|\Delta|^2) - a^2h^2(3 - 26|\Delta|^2 + 16|\Delta|^4) - 2|\Delta|^2a^4(1 - 8|\Delta|^2 + 16|\Delta|^4) \right] [\widehat{\Delta\Delta^*}]^2 \\
& \quad - \frac{4h}{(1 - 4|\Delta|^2)^2} \left[ h^4 - 3a^2h^2(1 - 8|\Delta|^2) + 8|\Delta|^2a^4 \right] [\widehat{\Delta\Delta^*}] [\Delta[\widehat{\Delta^*h}] - \Delta^*[\widehat{\Delta h}]] \\
& \quad + \frac{4}{(1 - 4|\Delta|^2)^2} \frac{a^2}{(h^2 + a^2)} \left[ h^4(1 - 26|\Delta|^2) + h^2a^2(3 - 16|\Delta|^2 - 64|\Delta|^4) + 2|\Delta|^2a^4 \right] \\
& \hspace{15em} \times [\Delta^{*2}[\widehat{\Delta h}]^2 + \Delta^2[\widehat{\Delta^*h}]^2] \\
& \quad - \frac{8|\Delta|^2}{(1 - 4|\Delta|^2)^2} \frac{a^2}{(h^2 + a^2)} \left[ h^4(6 - 14|\Delta|^2 + 12|\Delta|^4) \right. \\
& \quad \left. + 2h^2a^2(1 + 2|\Delta|^2 - 8|\Delta|^4 + 24|\Delta|^6) - 2|\Delta|^2a^4 \right] [\widehat{\Delta h}][\widehat{\Delta^*h}] \Big\} \\
& - \frac{\hbar^2(1 - 4|\Delta|^2)\sqrt{h^2 + a^2}}{8(h^2 + 4|\Delta|^2a^2)^{\frac{5}{2}}} \left\{ \frac{|\Delta|^2a^2}{h^2 + a^2} (2h^2 - 4|\Delta|^2a^2) (\widehat{hh}) \right. \\
& \quad - \frac{h}{1 - 4|\Delta|^2} (h^2 - 8|\Delta|^2a^2) [\Delta^*(\widehat{h\Delta}) + \Delta(\widehat{h\Delta^*})] \\
& \quad - \frac{8|\Delta|^2(h^2 + a^2)}{(1 - 4|\Delta|^2)^2} \left[ h^2(1 - |\Delta|^2) + |\Delta|^2a^2(1 - 4|\Delta|^2) \right] (\widehat{\Delta\Delta^*}) \\
& \quad \left. - \frac{2(h^2 + a^2)}{(1 - 4|\Delta|^2)^2} \left[ h^2(1 + 2|\Delta|^2) - 2|\Delta|^2a^2(1 - 4|\Delta|^2) \right] [\Delta^{*2}(\widehat{\Delta\Delta}) + \Delta^2(\widehat{\Delta^*\Delta^*})] \right\} \\
& + \frac{\hbar^2(1 - 4|\Delta|^2)\sqrt{h^2 + a^2}}{8(h^2 + 4|\Delta|^2a^2)^{\frac{7}{2}}} \left\{ \frac{2|\Delta|^2a^2h}{(h^2 + a^2)^2} \left[ 3h^4 + 2h^2a^2(1 - 6|\Delta|^2) + 8|\Delta|^2a^4(1 - 4|\Delta|^2) \right] (\widehat{h\Delta\Delta}) \right. \\
& \quad - \frac{2}{(1 - 4|\Delta|^2)} \frac{a^2}{(h^2 + a^2)} \left[ h^4(1 - 4|\Delta|^2) - 4|\Delta|^2h^2a^2(3 - 16|\Delta|^2) + 16|\Delta|^4a^4 \right] \\
& \hspace{15em} \times [\Delta^*(\widehat{h\Delta\Delta}) + \Delta(\widehat{h\Delta\Delta^*})] \\
& \quad + \frac{8|\Delta|^2h}{(1 - 4|\Delta|^2)^2} \left[ h^4(1 - 2|\Delta|^2) - h^2a^2(3 - 10|\Delta|^2 + 16|\Delta|^4) \right. \\
& \quad \left. - 2|\Delta|^2a^4(1 + 8|\Delta|^2 + 16|\Delta|^4) \right] (\widehat{h\Delta\Delta^*}) \\
& \quad + \frac{8\Delta|^2h}{(1 - 4|\Delta|^2)^2} \left[ h^4 - a^2h^2(5 - 8|\Delta|^2) + a^4(5 - 40|\Delta|^2 + 16|\Delta|^4) \right] \\
& \hspace{15em} \times [\Delta^{*2}(\widehat{h\Delta\Delta}) + \Delta^2(\widehat{h\Delta^*\Delta^*})] \\
& \quad + \frac{4|\Delta|^2}{(1 - 4|\Delta|^2)} \frac{a^2h^2}{(h^2 + a^2)} \left[ 7h^2 + a^2(5 + 8|\Delta|^2) \right] [\Delta^*(\widehat{\Delta hh}) + \Delta(\widehat{\Delta^*hh})] \\
& \quad + \frac{4|\Delta|^2h}{(1 - 4|\Delta|^2)^2} \left[ h^4 - a^2h^2(3 - 24|\Delta|^2) + 8|\Delta|^2a^4 \right] [(\widehat{\Delta h\Delta^*}) + (\widehat{\Delta^*h\Delta})]
\end{aligned}$$

$$\begin{aligned}
& + \frac{4h}{(1-4|\Delta|^2)^2} \left[ h^4 - a^2 h^2 (3 - 24|\Delta|^2) + 8|\Delta|^2 a^4 \right] \left[ \Delta^{*2}(\widehat{\Delta h \Delta}) + \Delta^2(\widehat{\Delta^* h \Delta^*}) \right] \\
& + \frac{8h^2(h^2 + a^2)}{(1-4|\Delta|^2)^3} \left[ h^2(1 + |\Delta|^2) - |\Delta|^2 a^2(1 - 24|\Delta|^2) \right] \left[ \Delta^*(\widehat{\Delta \Delta \Delta^*}) + \Delta(\widehat{\Delta^* \Delta \Delta^*}) \right] \\
& - \frac{4(h^2 + a^2)}{(1-4|\Delta|^2)^3} \left[ h^4(1 - 11|\Delta|^2 + 8|\Delta|^4) + |\Delta|^2 a^2 h^2(11 - 80|\Delta|^2 + 64|\Delta|^4) \right. \\
& \quad \left. + 8|\Delta|^4 a^4(1 - 8|\Delta|^2 + 16|\Delta|^4) \right] \left[ \Delta(\widehat{\Delta \Delta^* \Delta^*}) + \Delta^*(\widehat{\Delta^* \Delta \Delta}) \right] \\
& + \frac{4(h^2 + a^2)}{(1-4|\Delta|^2)^3} \left[ h^4(3 + 8|\Delta|^2) - a^2 h^2(3 - 16|\Delta|^2 - 64|\Delta|^4) \right. \\
& \quad \left. + 8|\Delta|^2 a^4(1 - 8|\Delta|^2 + 16|\Delta|^4) \right] \left[ \Delta^{*3}(\widehat{\Delta \Delta \Delta}) + \Delta^3(\widehat{\Delta^* \Delta^* \Delta^*}) \right] \Big\} \\
\end{aligned} \tag{257}$$

In the final step of the evaluation of Eq. (238) for  $\tau^{(2)}[n, \Delta]$ , we have to substitute Eqs. (256) and (257) into (255). The limit  $a \rightarrow 0$  is then calculated applying relations (246)–(249).

We now give the final expressions for the kinetic energy functional up to second order.

With

$$h = \frac{p^2}{2m} - \mu[n, \Delta](\mathbf{R}) \tag{258}$$

and

$$\mu[n, \Delta](\mathbf{R}) = \left( \int \frac{d^3 p}{(2\pi\hbar)^3} \left( 1 - \text{sign}(h) \sqrt{1 - 4|\Delta|^2} \right) \right)^{-1}, \tag{259}$$

we have

$$T_s^{(0)}[n, \Delta] = \int d^3 R \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} \left( 1 - \text{sign}(h) \sqrt{1 - 4|\Delta|^2} \right) \tag{260}$$

$$T_s^{(2)}[n, \Delta] = \int d^3 R \left( \tau^{(2)}[n, \Delta](\mathbf{R}) + \frac{\hbar^2}{2m} \frac{\nabla^2}{4} n(\mathbf{R}) \right) \tag{261}$$

where

$$\begin{aligned}
\tau^{(2)}[n, \Delta](\mathbf{R}) = \hbar^2 \int \frac{d^3 p}{(2\pi\hbar)^3} h \Big\{ & \text{sign}(h) \frac{2|\Delta|^2}{(1-4|\Delta|^2)^{\frac{3}{2}}} [\widehat{\Delta \Delta^*}]^2 \\
& + \frac{h\delta''(h)}{48|\Delta|^4} \frac{(5 - 52|\Delta|^2 - 16|\Delta|^4)}{(1-4|\Delta|^2)^{\frac{3}{2}}} \left( \Delta^{*2}[\widehat{\Delta h}]^2 + \Delta^2[\widehat{\Delta^* h}]^2 \right) \\
& - \frac{h\delta''(h)}{24|\Delta|^2} \frac{(7 - 12|\Delta|^2 + 16|\Delta|^4 + 64|\Delta|^6)}{(1-4|\Delta|^2)^{\frac{3}{2}}} [\widehat{\Delta h}][\widehat{\Delta^* h}] \\
& + \frac{1}{8} \delta'(h) \sqrt{1 - 4|\Delta|^2} (\widehat{hh}) \\
& - \frac{1}{4} \text{sign}(h) \frac{1 - 2|\Delta|^2}{(1-4|\Delta|^2)^{\frac{3}{2}}} (\widehat{\Delta \Delta^*}) \\
& - \frac{1}{4} \text{sign}(h) \frac{1}{(1-4|\Delta|^2)^{\frac{3}{2}}} \left[ \Delta^{*2}(\widehat{\Delta \Delta}) + \Delta^2(\widehat{\Delta^* \Delta^*}) \right] \\
& + \frac{1}{12} \delta''(h) \sqrt{1 - 4|\Delta|^2} (\widehat{hhh}) \\
\end{aligned}$$

$$\begin{aligned}
& - \frac{h\delta''(h)}{12|\Delta|^2} \frac{3-16|\Delta|^2}{\sqrt{1-4|\Delta|^2}} \left[ \Delta^* (\widehat{hh\Delta}) + \Delta (\widehat{hh\Delta}^*) \right] \\
& - \frac{h\delta''(h)}{24|\Delta|^2} \frac{3+4|\Delta|^2}{\sqrt{1-4|\Delta|^2}} \left[ \Delta^* (\widehat{\Delta hh}) + \Delta (\widehat{\Delta^* hh}) \right] \\
& - \text{sign}(h) \frac{1-2|\Delta|^2}{(1-4|\Delta|^2)^{\frac{5}{2}}} \left[ \Delta^* (\widehat{\Delta\Delta\Delta^*}) + \Delta (\widehat{\Delta^*\Delta\Delta^*}) \right] \\
& - \text{sign}(h) \frac{|\Delta|^2}{(1-4|\Delta|^2)^{\frac{5}{2}}} \left[ \Delta (\widehat{\Delta\Delta^*\Delta^*}) + \Delta^* (\widehat{\Delta^*\Delta\Delta}) \right] \\
& - \text{sign}(h) \frac{1}{(1-4|\Delta|^2)^{\frac{5}{2}}} \left[ \Delta^{*3} (\widehat{\Delta\Delta\Delta}) + \Delta^3 (\widehat{\Delta^*\Delta^*\Delta^*}) \right] \} .
\end{aligned} \tag{262}$$

#### 6.4 The normal-state limit

In this section we briefly check if the density functionals  $\tau^{(0)}[n, \Delta]$  and  $\tau^{(2)}[n, \Delta]$  correctly reduce to the known results for normal-state systems after the limiting process  $\Delta \rightarrow 0$ .

We first note that in this case we can explicitly calculate  $\mu[n]$ :

$$\begin{aligned}
\mu[n](\mathbf{R}) &= \lim_{\Delta \rightarrow 0} \left( \int \frac{d^3p}{(2\pi\hbar)^3} \left( 1 - \text{sign}(h) \sqrt{1-4|\Delta|^2} \right) \right)^{-1} \\
&= \left( 2 \int \frac{d^3p}{(2\pi\hbar)^3} \theta(-h) \right)^{-1} \\
&= \frac{(3\pi^2\hbar^3)^{\frac{2}{3}}}{2m} n(\mathbf{R})^{\frac{2}{3}}
\end{aligned} \tag{263}$$

where  $h = \frac{p^2}{2m} - \mu[n](\mathbf{R})$ . We therefore obtain:

$$\begin{aligned}
\tau^{(0)}[n](\mathbf{R}) &= \lim_{\Delta \rightarrow 0} \int \frac{d^3p}{(2\pi\hbar)^3} \frac{p^2}{2m} \left( 1 - \text{sign}(h) \sqrt{1-4|\Delta|^2} \right) \\
&= 2 \int \frac{d^3p}{(2\pi\hbar)^3} \frac{p^2}{2m} \theta(-h) \\
&= \frac{3\hbar^2(3\pi^2)^{\frac{2}{3}}}{10m} n(\mathbf{R})^{\frac{5}{3}}
\end{aligned} \tag{264}$$

$$\begin{aligned}
\tau^{(2)}[n](\mathbf{R}) &= \lim_{\Delta \rightarrow 0} \hbar^2 \int \frac{d^3p}{(2\pi\hbar)^3} \left\{ \frac{1}{8} h\delta'(h) \sqrt{1-4|\Delta|^2} (\widehat{hh}) \right. \\
&\quad \left. + \frac{1}{12} h\delta''(h) \sqrt{1-4|\Delta|^2} (\widehat{hhh}) \right\} \\
&= \hbar^2 \int \frac{d^3p}{(2\pi\hbar)^3} \left\{ \frac{1}{8} h\delta'(h) (\widehat{hh}) + \frac{1}{12} h\delta''(h) (\widehat{hhh}) \right\} \\
&= \hbar^2 \frac{\sqrt{2m}}{24\pi^2\hbar^3} \sqrt{\mu[n]} \nabla^2 \mu[n] + \hbar^2 \frac{\sqrt{2m}}{24\pi^2\hbar^3} \frac{(\nabla\mu[n])^2}{\sqrt{\mu[n]}} \\
&= \frac{\hbar^2}{24m} \nabla^2 n + \frac{\hbar^2}{72m} \frac{(\nabla n)^2}{n} .
\end{aligned} \tag{265}$$

Substituting into Eq. (209), we get the correct normal-state kinetic energy density up to second order:

$$t_s[n] = \frac{3\hbar^2(3\pi^2)^{\frac{2}{3}}}{10m} n^{\frac{5}{3}} + \frac{\hbar^2}{6m} \nabla^2 n + \frac{\hbar^2}{72m} \frac{(\nabla n)^2}{n} . \tag{266}$$



The first two terms of the gradient expansion (54) of  $T_s$  are recovered by integrating  $t_s$  over  $\mathbf{R}$ , see Eq. (152). Assuming that  $n(\mathbf{R})$  and its gradients vanish for  $R \rightarrow \infty$  on an appropriate surface, one can use Green's theorem to show that the second term on the right-hand side of Eq. (266) gives no contribution to  $T_s$ .

## 7 Variational principle: A Thomas-Fermi equation for superconductors

We now demonstrate how the HK variational equations (133) and (134) are established for our approximation of the kinetic energy functional  $T_s[n, \Delta]$  under neglect of exchange and correlation. In the following, only the zero-order term (260) is treated explicitly.

First we perform the variation with respect to  $n(\mathbf{R})$  in Eq. (133). Using Green's theorem, it follows that the second term under the integral on the right-hand side of Eq. (261) gives no contribution to  $T_s^{(2)}[n, \Delta]$ . As the gradient expansion of  $T_s[n, \Delta]$  therefore contains  $n(\mathbf{R})$  only implicitly via  $\mu[n, \Delta](\mathbf{R})$ , in analogy to the chain rule in elementary analysis the prescription for the variation reads:

$$\frac{\delta T_s[n, \Delta]}{\delta n(\mathbf{R})} = \int d^3 R' \frac{\delta T_s[\mu[n, \Delta], \Delta]}{\delta \mu(\mathbf{R}')} \frac{\delta \mu[n, \Delta](\mathbf{R}')}{\delta n(\mathbf{R})} \quad (267)$$

where

$$\frac{\delta \mu[n, \Delta](\mathbf{R}')}{\delta n(\mathbf{R})} = \frac{\delta(\mathbf{R}' - \mathbf{R})}{2 \int \frac{d^3 p}{(2\pi\hbar)^3} \delta(h) \sqrt{1 - 4|\Delta|^2}} \quad , \quad (268)$$

so that

$$\frac{\delta T_s^{(0)}[n, \Delta]}{\delta n(\mathbf{R})} = \mu[n, \Delta](\mathbf{R}) \quad . \quad (269)$$

We deal in a similar way with the variation by  $\Delta^*(\mathbf{R}, \mathbf{p})$  in Eq. (134). Because  $\Delta^*(\mathbf{R}, \mathbf{p})$  appears not only *implicitly*, but also *explicitly* in  $T_s[n, \Delta]$ , we write

$$\frac{\delta T_s[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} = \left. \frac{\delta T_s[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} \right|_{\text{partial}} + \int d^3 R' \frac{\delta T_s[\mu[n, \Delta], \Delta]}{\delta \mu(\mathbf{R}')} \frac{\delta \mu[n, \Delta](\mathbf{R}')}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} \quad . \quad (270)$$

With

$$\left. \frac{\delta T_s^{(0)}[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} \right|_{\text{partial}} = \frac{2\Delta(\mathbf{R}, \mathbf{p}) \text{sign}(h)}{(2\pi\hbar)^3 \sqrt{1 - 4|\Delta|^2}} \frac{p^2}{2m} \quad (271)$$

and

$$\frac{\delta \mu[n, \Delta](\mathbf{R}')}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} = - \frac{2\Delta(\mathbf{R}, \mathbf{p}) \text{sign}(h)}{(2\pi\hbar)^3 \sqrt{1 - 4|\Delta|^2}} \frac{\delta \mu[n, \Delta](\mathbf{R}')}{\delta n(\mathbf{R})} \quad , \quad (272)$$

we obtain up to second order:

$$\frac{\delta T_s[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} = \left. \frac{\delta T_s^{(2)}[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} \right|_{\text{partial}} + \frac{2\Delta(\mathbf{R}, \mathbf{p}) \text{sign}(h)}{(2\pi\hbar)^3 \sqrt{1 - 4|\Delta|^2}} \left( \frac{p^2}{2m} - \frac{\delta T_s[n, \Delta]}{\delta n(\mathbf{R})} \right) \quad . \quad (273)$$

The HK variational equations for superconductors, Eqs. (133) and (134), then lead to

$$\frac{\delta T_s[n, \Delta]}{\delta n(\mathbf{R})} = \mu - v_{ext}(\mathbf{R}) - e^2 \int d^3 R' \frac{n(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} \quad (274)$$

$$\begin{aligned} (2\pi\hbar)^3 \frac{\delta T_s^{(2)}[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} \Big|^{partial} &+ \frac{2\Delta(\mathbf{R}, \mathbf{p}) \text{sign}(h)}{\sqrt{1 - 4|\Delta|^2}} \left( \frac{p^2}{2m} - \frac{\delta T_s[n, \Delta]}{\delta n(\mathbf{R})} \right) \\ &= D_{ext}(\mathbf{R}, \mathbf{p}) + \int d^3 R' \int \frac{d^3 p'}{(2\pi\hbar)^3} w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}') \Delta(\mathbf{R}', \mathbf{p}') \quad . \end{aligned} \quad (275)$$

In a Thomas-Fermi-like theory, one usually proceeds by transforming the integral equation (274) for the normal density into a differential equation for the total electrostatic potential, which is achieved with the help of Poisson's equation.

For the superconducting case, it is convenient to perform an analogous transformation and change Eq. (275) for the anomalous density into an equation for an effective pair potential. As shown below, we will gain a formal generalization of the well-known BCS gap equation in this manner.

We begin with the definition of two quantities: the total electrostatic potential

$$\begin{aligned} u(\mathbf{R}) &\equiv \frac{\delta T_s[n, \Delta]}{\delta n(\mathbf{R})} \\ &= \mu - v_{ext}(\mathbf{R}) - e^2 \int d^3 R' \frac{n(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} \end{aligned} \quad (276)$$

and the effective pair potential

$$\mathcal{D}(\mathbf{R}, \mathbf{p}) \equiv \frac{2\Delta(\mathbf{R}, \mathbf{p})}{\sqrt{1 - 4|\Delta|^2}} \left( \frac{p^2}{2m} - u(\mathbf{R}) \right) \text{sign} \left( \frac{p^2}{2m} - u(\mathbf{R}) \right) \quad . \quad (277)$$

In order to express  $n(\mathbf{R})$  and  $\Delta(\mathbf{R}, \mathbf{p})$  as functionals of  $u(\mathbf{R})$  and  $\mathcal{D}(\mathbf{R}, \mathbf{p})$ , we first solve Eq. (277) for  $\Delta(\mathbf{R}, \mathbf{p})$  and obtain

$$\Delta[u, \mathcal{D}](\mathbf{R}, \mathbf{p}) = \frac{\mathcal{D}(\mathbf{R}, \mathbf{p})}{2 \sqrt{\left( \frac{p^2}{2m} - u(\mathbf{R}) \right)^2 - |\mathcal{D}(\mathbf{R}, \mathbf{p})|^2}} \quad . \quad (278)$$

Applying Poisson's equation to Eq. (276) we find

$$\begin{aligned} \nabla^2 u(\mathbf{R}) &= \nabla^2 (\mu - v_{ext}(\mathbf{R})) + 4\pi e^2 n(\mathbf{R}) \\ &\equiv 4\pi e^2 n_{ext}(\mathbf{R}) + 4\pi e^2 n(\mathbf{R}) \end{aligned} \quad (279)$$

and therefore

$$n[u](\mathbf{R}) = \frac{\nabla^2 u(\mathbf{R})}{4\pi e^2} - n_{ext}(\mathbf{R}) \quad . \quad (280)$$

In this fashion,  $h$  can be written as a functional of  $u$  and  $\mathcal{D}$ :

$$\begin{aligned} h[u, \mathcal{D}] &= \frac{p^2}{2m} - \mu[n[u], \Delta[u, \mathcal{D}]](\mathbf{R}) \\ &= \frac{p^2}{2m} - \mu[u, \mathcal{D}](\mathbf{R}) \quad , \end{aligned} \quad (281)$$

where  $\mu[u, \mathcal{D}](\mathbf{R})$  follows from solving

$$n[u](\mathbf{R}) = \int \frac{d^3 p}{(2\pi\hbar)^3} \left( 1 - \text{sign}\left(\frac{p^2}{2m} - \mu(\mathbf{R})\right) \sqrt{1 - 4|\Delta[u, \mathcal{D}]|^2} \right) \quad (282)$$

for  $\mu(\mathbf{R})$ , with  $\Delta[u, \mathcal{D}]$  given by Eq. (278) and  $n[u]$  given by Eq. (280).

We can now deduce the two equations for  $u$  and  $\mathcal{D}$  by performing the substitution (278) and (280) in Eqs. (275) and (276), and we get

$$u(\mathbf{R}) = \mu[u, \mathcal{D}](\mathbf{R}) + \left. \frac{\delta T_s^{(2)}[n, \Delta]}{\delta n(\mathbf{R})} \right|_{\substack{n=n[u] \\ \Delta=\Delta[u, \mathcal{D}]}} \quad (283)$$

$$\begin{aligned} \mathcal{D}(\mathbf{R}, \mathbf{p}) &= D_{ext}(\mathbf{R}, \mathbf{p}) + \frac{1}{2} \int d^3 R' \int \frac{d^3 p'}{(2\pi\hbar)^3} w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}') \frac{\mathcal{D}(\mathbf{R}', \mathbf{p}')}{\sqrt{\left(\frac{p^2}{2m} - u(\mathbf{R})\right)^2 + |\mathcal{D}|^2}} \\ &+ \left[ 1 - \text{sign}(h) \text{sign}\left(\frac{p^2}{2m} - u(\mathbf{R})\right) \right] \mathcal{D}(\mathbf{R}, \mathbf{p}) - (2\pi\hbar)^3 \left. \frac{\delta T_s^{(2)}[n, \Delta]}{\delta \Delta^*(\mathbf{R}, \mathbf{p})} \right|_{\substack{n=n[u] \\ \Delta=\Delta[u, \mathcal{D}]}}^{\text{partial}} \end{aligned} \quad (284)$$

If all terms of higher order than  $T_s^{(0)}$  are neglected, it is evident from (283) that  $u(\mathbf{R}) = \mu[u, \mathcal{D}](\mathbf{R})$ , and thus  $\frac{p^2}{2m} - u(\mathbf{R}) = h$ . Consequently, in the zero-order case, Eq. (284) reduces to a local version of the BCS gap equation:

$$\boxed{\mathcal{D}(\mathbf{R}, \mathbf{p}) = D_{ext}(\mathbf{R}, \mathbf{p}) + \frac{1}{2} \int d^3 R' \int \frac{d^3 p'}{(2\pi\hbar)^3} w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}') \frac{\mathcal{D}(\mathbf{R}', \mathbf{p}')}{\sqrt{h^2 + |\mathcal{D}|^2}}} \quad (285)$$

If we then take the normal-state limit of Eq. (283) and use Eq. (263), the classical Thomas-Fermi equation emerges:

$$\nabla^2 u(\mathbf{R}) = \frac{8\sqrt{2} e^2 u^{\frac{2}{3}}}{3\pi\hbar^3} + 4\pi e^2 n_{ext}(\mathbf{R}) \quad . \quad (286)$$

We note in summarizing that there are two alternative ways at our disposal to formulate the HK variational equations for superconductors: in terms of the densities  $n$  and  $\Delta$  or, on the other hand, in terms of the effective potentials  $u$  and  $\mathcal{D}$ .

As a first approach to solve these equations for a realistic superconductor, one could use a “good” potential  $u(\mathbf{R})$  (which can be obtained by performing a KS-calculation in the corresponding normal-state system) to calculate  $h = \frac{p^2}{2m} - u(\mathbf{R})$  and then, given this  $h$ , solve the gap equation (285) to determine  $\mathcal{D}(\mathbf{R}, \mathbf{p})$ .

Eq. (285) can also be obtained by taking the semiclassical limit of Gorkov’s equation for the Green’s function (Bruder 1990). Our derivation has the advantage that it allows for the systematic inclusion of inhomogeneity corrections and of xc contributions.

An interesting application consists in setting  $w(\mathbf{R}, \mathbf{p}, \mathbf{R}', \mathbf{p}')$  in (284) equal to zero. The existence of a solution of the resulting differential equation would be an indication of purely coulombic, inhomogeneity-induced superconductivity.

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	LDA	BLYP	PW91	OPM	CI	EXACT
He	2.833	2.9071	2.9000	2.9033	2.9049	2.9037
Li	7.343	7.4827	7.4742	7.4829	7.4743	7.4781
Be	14.446	14.6615	14.6479	14.6651	14.6657	14.6674
B	24.352	24.6458	24.6299	24.6564	24.6515	24.6539
C	37.466	37.8430	37.8265	37.8490	37.8421	37.8450
N	54.129	54.5932	54.5787	54.5905	54.5854	54.5893
O	74.521	75.0786	75.0543	75.0717	75.0613	75.067
F	99.108	99.7581	99.7316	99.7302	99.7268	99.734
Ne	128.227	128.9730	128.9466	128.9202	128.9277	128.939
$\bar{\Delta}$	0.384	0.0108	0.0114	0.0047	0.0045	

Table 1: *Total absolute ground-state energies for first-row atoms from various self-consistent calculations. CI values from Montgomery et al. (1994).  $\bar{\Delta}$  denotes the mean absolute deviation from the exact nonrelativistic value (Davidson et al. 1991). All numbers in Hartree units.*

## References

- Antoniewicz, P. R., and Kleinman, L. (1985). *Phys. Rev. B* **31**, 6779.
- Baraff, G. A., and Borowitz, S. (1961). *Phys. Rev.* **121**, 1704.
- Bardeen, J., Cooper, L. N., and Schrieffer, J. R. (1957). *Phys. Rev.* **108**, 1175.
- Barth, U. von, and Hedin, L. (1972). *J. Phys. C* **5**, 1629.
- Becke, A. D. (1986). *J. Chem. Phys.* **84**, 4524.
- Becke, A. D. (1988). *Phys. Rev. A* **38**, 3098.
- Bishop, R. F., and Lührmann, K. H. (1978). *Phys. Rev. B* **17**, 3757.
- Bishop, R. F., and Lührmann, K. H. (1982). *Phys. Rev. B* **26**, 5523.
- Bruder, C. (1990). *Phys. Rev. B* **41**, 4017.
- Ceperley, D. M., and Alder, B. J. (1980). *Phys. Rev. Lett.* **45**, 566.
- Chevary, J. A., and Vosko, S. H. (1988). *Bull. Am. Phys. Soc.* **33**, 238.
- Cole, L. A., and Perdew, J. P. (1982). *Phys. Rev. A* **25**, 1265.
- Colle, R., and Salvetti, D. (1975). *Theor. Chim. Acta* **37**, 329.
- Colle, R., and Salvetti, D. (1979). *Theor. Chim. Acta* **53**, 55.
- Davidson, E. R., Hagstrom, S. A., Chakravorty, S. J., Umar, V. M., and Froese-Fischer, C. (1991). *Phys. Rev. A* **44**, 7071.
- DePristo, A. E., and Kress, J. D. (1987). *J. Chem. Phys.* **86**, 1425.
- Dirac, P. A. M. (1930). *Proc. Cambridge Phil. Soc.* **26**, 376.
- Dobson, J. F. (1991). *J. Chem. Phys.* **94**, 4328.
- Dobson, J. F. (1992). *J. Phys.: Condens. Matter* **4**, 7877.
- Dobson, J. F. (1993). *J. Chem. Phys.* **98**, 8870.
- Dobson, J. F., and Rose, J. H. (1982). *J. Phys. C* **15**, L1183.
- Dreizler, R. M., and Gross, E. K. U. (1990). 'Density Functional Theory: An Approach to the Quantum Many-Body Problem' (Springer: Berlin).
- Dufek, P., Blaha, P., and Schwarz, K. (1994). *Phys. Rev. B* **50**, 7279.
- Engel, E., Chevary, J. A., MacDonald, L. D., and Vosko, S. H. (1992). *Z. Phys. D* **23**, 7.
- Engel, E., and Vosko, S. H. (1990). *Phys. Rev. B* **42**, 4940.
- Engel, E., and Vosko, S. H. (1993a). *Phys. Rev. A* **47**, 2800.
- Engel, E., and Vosko, S. H. (1993b). *Phys. Rev. B* **47**, 13164.
- Fermi, E. (1928). *Z. Phys.* **48**, 73.
- Geldart, D. J. W., and Rasolt, M. (1976). *Phys. Rev. B* **13**, 1477.
- Geldart, D. J. W., and Rasolt, M. (1987). In 'The Single-Particle Density in Physics and Chemistry' (Eds N. H. March and B. M. Deb) pp. 151 ff. (Academic: London).
- Gell-Mann, M., and Brueckner, K. A. (1957). *Phys. Rev.* **106**, 364.
- Gennes, P. G. de (1966). 'Superconductivity of Metals and Alloys' (Benjamin: New York).
- Gill, P. M. W., Johnson, B. G., Pople, J. A., and Frisch, M. J. (1992). *Chem. Phys. Lett.* **197**, 499.
- Ginzburg, V. L., and Landau, L. D. (1950). *Zh. Eksperim. i Teor. Fiz.* **20**, 1064.
- Gorkov, L. P. (1959). *Sov. Phys. JEPT* **9**, 1364.

- Grabo, T., and Gross, E. K. U. (1995). *Chem. Phys. Lett.* **240**, 141.
- Grammaticos, B., and Voros, A. (1979). *Ann. Phys. New York* **123**, 359.
- Gross, E. K. U., and Dreizler, R. M. (1981). *Z. Phys. A* **302**, 103.
- Gross, E. K. U., and Dreizler, R. M. (Eds) (1994). 'Density Functional Theory', NATO ASI Series B337 (Plenum: New York).
- Gross, E. K. U., and Kohn, W. (1985). *Phys. Rev. Lett.* **55**, 2850 [erratum *ibid.* (1986) **57**, 923].
- Gross, E. K. U., and Kohn, W. (1990). *Adv. Quant. Chem.* **21**, 255.
- Gross, E. K. U., and Kurth, S. (1991). *Int. J. Quant. Chem. Symp.* **25**, 289.
- Gross, E. K. U., and Kurth, S. (1993). In 'Relativistic and Electron Correlation Effects in Molecules and Solids' (Ed. G. L. Malli), NATO ASI Series B318, pp. 367 ff. (Plenum: New York).
- Gross, E. K. U., Kurth, S., Capelle, K., and Lüders, M. (1994). In 'Density Functional Theory' (Eds E. K. U. Gross and R. M. Dreizler), NATO ASI Series B337, pp. 431 ff. (Plenum: New York).
- Gross, E. K. U., Petersilka, M., and Grabo, T. (1996). In 'Density Functional Methods in Chemistry', ACS, in press.
- Hanke, W., Meskini, N., and Weiler, H. (1985). In 'Electronic Structure, Dynamics, and Quantum Structural Properties of Condensed Matter' (Eds J. T. Devreese and P. Van Camp), NATO ASI Series B121, pp. 113 ff. (Plenum: New York).
- Harriman, J. E. (1981). *Phys. Rev. A* **24**, 680.
- Harrison, J. G., Heaton, R. A., and Lin, C. C. (1983). *J. Phys. B* **16**, 2079.
- Heaton, R. A., Harrison, J. G., and Lin, C. C. (1983). *Phys. Rev. B* **28**, 5992.
- Hohenberg, P., and Kohn, W. (1964). *Phys. Rev.* **136**, B864.
- Hu, C. D., and Langreth, D. C. (1985). *Phys. Script.* **32**, 391.
- Hu, C. D., and Langreth, D. C. (1986). *Phys. Rev. B* **33**, 943.
- Johnson, B. G., Gill, P. M. W., and Pople, J. A. (1992). *J. Chem. Phys.* **97**, 7846.
- Johnson, B. G., Gill, P. M. W., and Pople, J. A. (1993). *J. Chem. Phys.* **98**, 5612.
- Juan, Y.-M., and Kaxiras, E. (1993). *Phys. Rev. B* **48**, 14944.
- Kalia, R. K., and Vashishta, P. (1978). *Phys. Rev. B* **17**, 2655.
- Kirzhnits, D. A. (1957). *Sov. Phys. JETP* **5**, 64.
- Kirzhnits, D. A. (1967). 'Field Theoretical Methods in Many-Body Systems' (Pergamon: London).
- Kleinman, L. (1984). *Phys. Rev. B* **30**, 2223.
- Kleinman, L., and Lee, S. (1988). *Phys. Rev. B* **37**, 4634.
- Kohn, W. (1985). In 'Highlights of Condensed Matter Theory' (Eds F. Bassani, F. Fumi, and M. P. Tosi) pp. 1 ff. (North-Holland: Amsterdam).
- Kohn, W. (1986). *Phys. Rev. B* **33**, 4331.
- Kohn, W., Gross, E. K. U., and Oliveira, L. N. (1989). *J. de Physique (Paris)* **50**, 2601.

- Kohn, W., and Sham, L. J. (1965). *Phys. Rev.* **140**, A1133.
- Kohn, W., and Vashishta, P. (1983). In 'Theory of the Inhomogeneous Electron Gas' (Eds S. Lundqvist and N. H. March) pp. 79 ff. (Plenum: New York).
- Krieger, J. B., Li, Y., and Iafrate, G. J. (1992). *Phys. Rev. A* **45**, 101.
- Langreth, D. C., and Mehl, M. J. (1981). *Phys. Rev. Lett.* **47**, 446.
- Langreth, D. C., and Mehl, M. J. (1983). *Phys. Rev. B* **28**, 1809 [erratum *ibid.* (1984) **29**, 2310].
- Langreth, D. C., and Perdew, J. P. (1975). *Sol. State Comm.* **17** 1425.
- Langreth, D. C., and Perdew, J. P. (1977). *Phys. Rev. B* **15**, 2884.
- Langreth, D. C., and Perdew, J. P. (1979). *Sol. State Comm.* **31**, 567.
- Langreth, D. C., and Perdew, J. P. (1980). *Phys. Rev. B* **21**, 5649.
- Langreth, D. C., and Perdew, J. P. (1982). *Phys. Rev. B* **26**, 2810.
- Lee, C., Yang, W., and Parr, R. G. (1988). *Phys. Rev. B* **37**, 785.
- Levy, M. (1979). *Proc. Natl. Acad. Sci. USA* **76**, 6062.
- Lieb, E. H. (1982). In 'Physics as Natural Philosophy' (Eds A. Shimony and H. Feshbach) pp. 111 ff. (MIT Press: Cambridge).
- Lieb, E. H. (1983). *Int. J. Quant. Chem.* **24**, 243.
- Lieb, E. H. (1985). In 'Density Functional Methods in Physics' (Eds R. M. Dreizler and J. da Providencia), NATO ASI Series B123, pp. 31 ff. (Plenum: New York).
- Ma, S. K., and Brueckner, K. A. (1968). *Phys. Rev.* **165**, 18.
- MacDonald, A. H., and Vosko, S. H. (1979). *J. Phys. C* **12**, 2977.
- Mahan, G. D., and Subbaswamy, K. R. (1990). 'Local Density Theory of Polarizability' (Plenum: New York).
- Mermin, N. D. (1965). *Phys. Rev.* **137**, A1441.
- Miehlich, B., Savin, A., Stoll, H., and Preuss, H. (1989). *Chem. Phys. Lett.* **157**, 200.
- Montgomery, J. A., Ochterski, J. W., and Pertersson, G. A. (1994). *J. Chem. Phys.* **101**, 5900.
- Nambu, Y. (1960). *Phys. Rev.* **117**, 648.
- Norman, M. R., and Koelling, D. D. (1984). *Phys. Rev. B* **30**, 5530.
- Oliveira, L. N., Gross, E. K. U., and Kohn, W. (1988). *Phys. Rev. Lett.* **60**, 2430.
- Perdew, J. P. (1979). *Chem. Phys. Lett.* **64**, 127.
- Perdew, J. P. (1985). In "Density Functional Methods in Physics" (Eds R. M. Dreizler and J. da Providencia), NATO ASI Series B123, pp. 265 ff. (Plenum: New York).
- Perdew, J. P. (1986a). *Int. J. Quant. Chem. Symp.* **19**, 497.
- Perdew, J. P. (1986b). *Phys. Rev. B* **33**, 8822 (erratum *ibid.* B **34**, 7406).
- Perdew, J. P. (1991). In 'Electronic Structures of Solids '91' (Eds P. Ziesche and H. Eschrig) (Akademie-Verlag: Berlin).
- Perdew, J. P., and Levy, M. (1983). *Phys. Rev. Lett.* **51**, 1884.
- Perdew, J. P., Parr, R. G., Levy, M., and Balduz, J. L. (1982). *Phys. Rev. Lett.* **49**, 1691.
- Perdew, J. P., and Wang, Y. (1986). *Phys. Rev. B* **33**, 8800.

- Perdew, J. P., and Wang, Y. (1992). *Phys. Rev. B* **45**, 13244.
- Perdew, J. P., and Zunger, A. (1981). *Phys. Rev. B* **23**, 5048.
- Pople, J. A., Gill, P. M. W., and Johnson, B. G. (1992), *Chem. Phys. Lett.* **199**, 557.
- Rajagopal, A. K. (1978). *J. Phys. C* **11**, L943.
- Rajagopal, A. K., and Callaway, J. (1973). *Phys. Rev. B* **7**, 1912.
- Ramana, M. V., and Rajagopal, A. K. (1983). *Adv. Chem. Phys.* **54**, 231.
- Rasolt, M. and Geldart, D. J. W. (1975). *Phys. Rev. Lett.* **35**, 1234.
- Rasolt, M. and Geldart, D. J. W. (1986). *Phys. Rev. B* **34**, 1325.
- Runge, E., and Gross, E. K. U. (1984). *Phys. Rev. Lett.* **52**, 997.
- Sander, L. M., Shore, H. B., and Sham, L. J. (1973). *Phys. Rev. Lett.* **31**, 533.
- Sham, L. J. (1971). In 'Computational Methods in Band Theory' (Eds P. J. Marcus, J. F. Janak, and A. R. Williams) pp. 458 ff. (Plenum: New York).
- Sham, L. J. (1985). *Phys. Rev. B* **32**, 3876.
- Sham, L. J., and Schlüter, M. (1983). *Phys. Rev. Lett.* **51**, 1888.
- Sham, L. J., and Schlüter, M. (1985). *Phys. Rev. B* **32**, 3883.
- Sharp, R. T., and Horton, G. K. (1953). *Phys. Rev.* **90**, 317.
- Svane, A. (1994). *Phys. Rev. Lett.* **72**, 1248.
- Svane, A., and Gunnarson, O. (1990). *Phys. Rev. Lett.* **65**, 1148.
- Szotek, Z., Temmerman, W. M., and Winter, H. (1993). *Phys. Rev. B* **47**, 4092.
- Szotek, Z., Temmerman, W. M., and Winter, H. (1994). *Phys. Rev. Lett.* **72**, 1244.
- Taruishi, K., and Schuck, P. (1992). *Z. Phys. A* **342**, 397.
- Talman, J. D., and Shadwick, W. F. (1976). *Phys. Rev. A* **14**, 36.
- Temmerman, W. M., Szotek, Z., and Winter, H. (1993). *Phys. Rev. B* **47**, 11533.
- Theis, W. R. (1955). *Z. Phys.* **142**, 503.
- Thomas, L. H. (1927). *Proc. Cambridge Phil. Soc.* **23**, 542.
- Ullrich, C. A., Gossmann, U. J., and Gross, E. K. U. (1995). *Phys. Rev. Lett.* **74**, 872.
- Vignale, G., and Rasolt, M. (1987). *Phys. Rev. Lett.* **59**, 2360.
- Vignale, G., and Rasolt, M. (1988). *Phys. Rev. B* **37**, 10685.
- Vosko, S. H., Wilk, L., and Nusair, M. (1980). *Can. J. Phys.* **58**, 1200.
- Vosko, S. H., and MacDonald, L. D. (1987). In 'Condensed Matter Theories, Vol. 2' (Eds P. Vashishta, R. K. Kalia, and R. F. Bishop) pp. 101 ff. (Plenum: New York).
- Wacker, O.-J., Kümmel, R., and Gross, E. K. U. (1994). *Phys. Rev. Lett.* **73**, 2915.
- Wilson, L. C., and Levy, M. (1990). *Phys. Rev. B* **41**, 12930.
- Weizsäcker, C. F. von (1935). *Z. Phys.* **96**, 431.
- Wigner, E. P. (1932). *Phys. Rev.* **40**, 749.
- Wigner, E. P. (1934). *Phys. Rev.* **46**, 1002.
- Wigner, E. P. (1938). *Trans. Farad. Soc.* **34**, 678.
- Zhu, T., Lee, C., and Yang, W. (1992). *J. Chem. Phys.* **98**, 4814.
- Zumbach, G., and Maschke, K. (1983). *Phys. Rev. A* **28**, 544 [erratum *ibid.* (1984) **29**, 1585].