

DENSITY FUNCTIONAL THEORY, THE MODERN TREATMENT OF ELECTRON CORRELATIONS

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1 INTRODUCTION

The basic idea of density functional theory is to describe a many-electron system exclusively and completely in terms of its ground-state density, i.e., in terms of the ordinary one-particle density (not the density matrix). This means two things:

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 section 2 of this review we will briefly indicate a proof of these two important statements first given by Hohenberg and Kohn [1]. The variational principle, i.e. statement (2) above, 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 [2], is the heart of modern density functional theory. The derivation and implications of this scheme will be discussed in detail in section 2 of this review.

The original theorems of Hohenberg and Kohn and Kohn and Sham refer to time-independent systems in a normal (i.e. non-superconducting) ground state. In the

remaining sections of this paper we shall describe three recent extensions of density functional theory, referring to excited states (section 3), to time-dependent external potentials (section 4), and to superconducting systems (section 5). With these extensions, density functional theory covers practically all situations of physical interest.

In this review, we will concentrate on the formalism of density functional theory and its implications. We shall not describe applications in great detail. For a comprehensive survey of applications to atoms, molecules and solids (until 1989) the reader is referred to the review article by Jones and Gunnarsson [3]. More recent applications to molecules are presented in the article by Salahub in this volume. For a critical review of the performance of density functional theory on 32 neutral molecules, the reader is referred to the recent work of Johnson, Gill, and Pople [4]. A survey of applications of time-dependent density functional theory can be found in the review article by Gross and Kohn [5] and in the book by Mahan and Subbaswamy [6].

2 DENSITY FUNCTIONAL THEORY OF THE GROUND STATE

2.1 The Theorems of Hohenberg and Kohn, and Kohn and Sham

We begin with a short summary of the original Hohenberg-Kohn (HK) theorem [1].

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 quantised notation, is given by

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

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

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

(Atomic units are used throughout.) For simplicity we consider only potentials $v(\mathbf{r})$ leading to a non-degenerate ground state Ψ (extension of the HK theorem to degenerate ground states is straightforward [7, 8]):

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

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 Ψ of (5). For each Ψ 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

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

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

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

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

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

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

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

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

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

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 the density

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

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 $n(\mathbf{r})$ [9, 10], 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

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

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 Φ (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

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

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

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

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 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

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

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

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

As a consequence, the Euler equation

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

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

Writing

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

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

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

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 [11, 12].

The variational principle of HK allows us to determine the ground-state density of a given many-electron system. Kohn and Sham [2] established a scheme which yields the exact ground-state density via an intermediary orbital picture. The equations read as follows

$$\left(-\frac{\nabla^2}{2} + v_s[n](\mathbf{r})\right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad (24)$$

$$n(\mathbf{r}) = \sum_{\text{lowest } N} |\varphi_j(\mathbf{r})|^2 \quad (25)$$

where $v_s[n](\mathbf{r})$ is a **local**, density-dependent single-particle potential. It is local in the sense of being a multiplicative operator in configuration space. The density dependence is non-local in general. In terms of the universal exchange-correlation (xc) energy $E_{xc}[n]$ (to be defined below), $v_s[n]$ can be written as

$$v_s(\mathbf{r}) = v_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (26)$$

Equations (24) to (26) have to be solved in a self-consistent fashion.

To prove the Kohn-Sham (KS) theorem (24) - (26) we first consider a system of **non-interacting** electrons with density $n_s(\mathbf{r})$, characterized by the Hamiltonian

$$\hat{H}_s = \sum_{\sigma=\uparrow\downarrow} \int d^3\mathbf{r} \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right) \hat{\psi}_\sigma(\mathbf{r}). \quad (27)$$

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

$$E_{v_s}^{\text{non-int}}[n] = T_s[n] + \int d^3\mathbf{r}' n(\mathbf{r}') v_s(\mathbf{r}'). \quad (28)$$

The HK variational principle (21) then reads

$$\begin{aligned} 0 &= \frac{\delta}{\delta n(\mathbf{r})} \left[E_{v_s}^{\text{non-int}}[n] - \mu \int d^3\mathbf{r}' n(\mathbf{r}') \right] \\ &= \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v_s(\mathbf{r}) - \mu. \end{aligned} \quad (29)$$

Eq. (29) 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

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad (30)$$

$$n_s(\mathbf{r}) = \sum_{\text{lowest } N} |\varphi_j(\mathbf{r})|^2. \quad (31)$$

The two ways of calculating n_s , either from (29) or from (30), (31), 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

$$E_v[n] = T[n] + U[n] + \int d^3\mathbf{r} n(\mathbf{r})v(\mathbf{r}). \quad (32)$$

By addition and subtraction we can write

$$\begin{aligned} E_v[n] &= T_s[n] \\ &+ \int d^3\mathbf{r} n(\mathbf{r})v(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n] \end{aligned} \quad (33)$$

where the xc-energy functional is defined as

$$E_{xc}[n] = T[n] - T_s[n] + U[n] - \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (34)$$

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

$$\frac{\delta T_s[n]}{\delta n(\mathbf{r})} + \left(v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \right) = \mu. \quad (35)$$

Eq. (35) is formally identical with the Euler equation (29) of non-interacting particles moving in the effective single-particle potential

$$v_s(\mathbf{r}) = v_0(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}[n](\mathbf{r}) \quad (36)$$

with

$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (37)$$

As (29) and (30), (31) were completely equivalent methods of calculating the density, we can, instead of using eq. (35), calculate the exact ground-state density via the Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + v_s[n](\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad (38)$$

$$n(\mathbf{r}) = \sum_{\text{lowest } N} |\varphi_j(\mathbf{r})|^2. \quad (39)$$

These are the Kohn-Sham equations. The proof shows that the KS scheme 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

$$\begin{aligned} T_s[n] &= \sum_j \int d^3\mathbf{r} \varphi_j^*(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \varphi_j(\mathbf{r}) \\ &= \sum_j \int d^3\mathbf{r} \varphi_j^*(\mathbf{r}) (\varepsilon_j - v_s[n](\mathbf{r})) \varphi_j(\mathbf{r}) \\ &= \sum_j \varepsilon_j - \int d^3\mathbf{r} n(\mathbf{r})v_s[n](\mathbf{r}) \end{aligned} \quad (40)$$

Insertion in eq. (33) leads to the following exact representation of the ground-state energy:

$$E_{gs} = \sum_{j=1}^N \varepsilon_j - \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3\mathbf{r} n(\mathbf{r}) v_{xc}[n](\mathbf{r}) + E_{xc}[n]. \quad (41)$$

By virtue of eq. (40) 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

$$F[n] = T_s[n] + E_{xc}[n] + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (42)$$

needs to be approximated. Direct use of the HK variational principle (21), on the other hand, requires approximations for the complete functional $F[n]$ which, in practice, are much harder to find than approximations for the xc part alone. Therefore it is always 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 φ_j must not be interpreted as an approximation for the true many-particle ground state. Only the densities calculated via the KS scheme and the total energies obtained from (41) are identical with the exact ground-state densities and energies.

At first sight, it appears rather surprising, that exchange, being an intrinsically non-local phenomenon, can be treated **exactly** with a **local** potential. As a matter of fact, one can prove HK- and KS-type theorems for the Hartree-Fock (HF) limit itself [13]. As a consequence of these theorems, the HF density and the total HF ground-state energy can be reproduced exactly with an “x-only KS” scheme

$$\left(-\frac{\nabla^2}{2} + v_0(\mathbf{r}) + \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{x\text{-only}}[n](\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad (43)$$

$$n(\mathbf{r}) = \sum_{\text{lowest } N} |\varphi_j(\mathbf{r})|^2. \quad (44)$$

Like in ordinary density functional theory, the exact potential $v_{x\text{-only}}(\mathbf{r})$ is not known. However, a very good approximation to it can be constructed, using the so-called optimized potential method (OPM) first introduced by Talman and Shadwick [14]. This method determines the “variationally best” local exchange-only potential, denoted by $v_{x\text{-only}}^{\text{OPM}}(\mathbf{r})$; “best” in the sense that the orbitals resulting from (43) minimize the usual HF energy functional $E_{HF}[\varphi_1, \dots, \varphi_N]$. This leads to an integral equation for $v_{x\text{-only}}^{\text{OPM}}(\mathbf{r})$ which has to be solved self-consistently with eq.(43). The single-particle orbitals obtained in this way are practically identical with the corresponding HF orbitals. Total atomic OPM ground-state energies are within 0.004 % of HF ground-state energies and the agreement of total exchange energies is better than 0.04 %. For a detailed analysis the reader is referred to [15]. This shows that the HF exchange energy is well reproduced with a local exchange potential. One has to emphasize, however, that the OPM is mainly of academic, not of practical interest because the numerical solution of the OPM equations is more involved than the solution of the HF equations. A simplified OPM scheme, however, has been proposed by Krieger and co-workers [16, 17].

We finally mention, that the traditional HK and KS theorems are easily extended to a wide variety of cases of physical interest, e.g. to spin-polarized systems [18, 19], multi-component systems [20, 21], thermal ensembles [22] and relativistic systems [19, 23, 24, 25].

Until now we have proven 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 for the xc-energy functional.

2.2 Approximations for the Exchange-Correlation Functional

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

$$E_{xc}^{LDA}[n] = \int d^3\mathbf{r} e_{xc}^{hom}(n(\mathbf{r})) \quad (45)$$

which leads to

$$v_{xc}^{LDA}[n](\mathbf{r}) = \frac{\delta E_{xc}^{LDA}[n]}{\delta n(\mathbf{r})} = \left. \frac{de_{xc}^{hom}(n)}{dn} \right|_{n=n(\mathbf{r})}. \quad (46)$$

$e_{xc}^{hom}(n)$ 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)

$$E_{xc}^{LSD}[n_{\uparrow}, n_{\downarrow}] = \int d^3\mathbf{r} e_{xc}^{hom}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) \quad (47)$$

where

$$n_{\sigma}(\mathbf{r}) = \sum_{\text{occupied}} |\varphi_{i\sigma}(\mathbf{r})|^2, \quad \sigma = \uparrow\downarrow. \quad (48)$$

In practical calculations one uses parametrizations for e_{xc}^{hom} . Currently the best parametrizations available are the one by Vosko, Wilk and Nusair [26] and the one by Perdew and Zunger [27].

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 :

$$E_{gap} = I - A = E_{gs}(N + 1) - 2E_{gs}(N) + E_{gs}(N - 1). \quad (49)$$

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 [28] - [36] 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 (49), these discontinuities need to be taken into account. One obtains the exact formula (see, e.g. [7], chapter 6.3)

$$E_{gap} = \varepsilon_C - \varepsilon_V + \lim_{\delta \rightarrow 0^+} (v_{xc}|_{N+\delta} - v_{xc}|_{N-\delta}) \quad (50)$$

where ε_V is the highest KS orbital energy of the valence band while ε_C is the lowest KS energy of the conduction band. Since v_{xc}^{LDA} is a continuous function of N , the last term of (50) vanishes within the LDA and the gap is poorly reproduced.

Besides that, the LDA (as well as the LSD) is deficient in two respects. First, the LDA does not contain any gradients of the density. A systematic way of constructing functionals containing density gradients is the so-called gradient expansion [1]. The first term of this expansion for the exchange-only part was calculated by Sham [37] and later corrected by Kleinman and collaborators [38, 39, 40], Chevary and Vosko [41] and Engel and Vosko [42]. The correct result is

$$E_x^{[1]}[n] = \int d^3\mathbf{r} c \frac{(\nabla n(\mathbf{r}))^2}{n(\mathbf{r})^{4/3}}, \quad c = -\frac{5}{216\pi(3\pi^2)^{1/3}}. \quad (51)$$

The calculation of the first term of the gradient expansion of the correlation energy functional has turned out to be an extremely difficult task. Many authors contributed to its calculation: Ma and Brueckner [43], Geldart and Rasolt [44] - [47], Langreth and Perdew [48] - [52], Langreth and Mehl [53, 54], and Hu and Langreth [55, 56]. The analytic structure of this term is as follows:

$$E_c^{[1]}[n] = \int d^3\mathbf{r} f(n(\mathbf{r})) \frac{(\nabla n(\mathbf{r}))^2}{n(\mathbf{r})^{4/3}}. \quad (52)$$

By now the **function** $f(n)$ is well known for the densities relevant in atoms, molecules and solids. For a comparison of different results for $f(n)$, the reader is referred to [7], chapter 7.6. The currently best functionals involving density gradients are the so-called generalized gradient approximations [57] - [63], [4], [15], which can be viewed as heuristic resummations of the gradient expansion. In all systems tested until now, the generalized gradient approximations performed better than the LSD [4, 62].

The second deficiency of the local approximations is the self-interaction error, arising from the fact that the self-Coulomb energy contained in

$$E_H[n] = \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (53)$$

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 $-\frac{1}{r}$ for neutral atoms and molecules. A self-interaction

corrected (SIC) functional for the xc energy was proposed by Perdew and Zunger [64, 27]:

$$\begin{aligned}
E_{xc}^{SIC}[n_{\uparrow}, n_{\downarrow}] &= E_{xc}^{LSD}[n_{\uparrow}, n_{\downarrow}] \\
&- \sum_i \left(E_H[n_{i\uparrow}] + E_{xc}^{LSD}[n_{i\uparrow}, 0] \right) \\
&- \sum_i \left(E_H[n_{i\downarrow}] + E_{xc}^{LSD}[0, n_{i\downarrow}] \right)
\end{aligned} \tag{54}$$

with

$$n_{i\sigma}(\mathbf{r}) = |\varphi_{i\sigma}(\mathbf{r})|^2. \tag{55}$$

This approximation yields definite improvement over the LSD, even for the band gap of insulators. A drawback of this functional is the fact that the single-particle potential appearing in the SIC-KS equations is a different one for each orbital.

To summarize, 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 for 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 [65], one needs the low-density limit known as the Wigner crystal [66, 67] and, for the intermediate density regime, quantum Monte Carlo computations [68] and/or many-body perturbation theory beyond RPA [69, 70] is required. Finally, all these data have to be put together in a reliable parametrization [26, 27]. 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 for $E_{xc}[n]$ 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 big systems for which the traditional methods of quantum chemistry are prohibitive.

3 DENSITY FUNCTIONAL THEORY FOR EXCITED STATES

As a consequence of the HK theorem, every quantum mechanical observable, in particular also excitation energies, can be calculated from the **ground state** density. Therefore, from a purist's point of view, the density functional formalism as described in the last section already provides a formal access to the calculation of excitation energies. This approach, however, cannot be used in practice because no explicit approximations are known for the functionals $E_{excited}[n]$ corresponding to excited-state energies. In particular, the KS single-particle energies cannot be interpreted as excited-state energies, with one exception: The highest occupied KS eigenvalue $\varepsilon_{highest}$ is identical with the exact ionization potential I . This statement follows from the asymptotic behaviour of the KS density

$$n_s(\mathbf{r}) = \sum_{lowest N} |\varphi_j(\mathbf{r})|^2 \xrightarrow{r \rightarrow \infty} |\varphi_{highest}(\mathbf{r})|^2 \longrightarrow \exp(-2\sqrt{-2\varepsilon_{highest}}r) \tag{56}$$

and from the fact that the exact density (resulting from the many-particle Schrödinger equation) behaves as

$$n(\mathbf{r}) \xrightarrow{r \rightarrow \infty} \exp(-2\sqrt{-2I}r). \quad (57)$$

Since, by virtue of the KS theorem, n_s and n are identical one finds by comparison of (56) with (57)

$$\varepsilon_{highest} = I. \quad (58)$$

Apart from this case, no prescription for calculating excitation energies from the ground-state density is available.

The traditional HK theorem only offers the indirect way of calculating the excitation energy from the **ground-state** density. An attractive alternative would be a HK variational principle for the **excited-state** energy itself, involving the density of the **excited state**.

Since the HK variational principle is essentially a reformulation of the Rayleigh-Ritz principle, one first needs to look for a Rayleigh-Ritz principle for excited states. Such a variational principle is well known; it requires, however, orthogonality of the trial functions to the **exact** lower eigenstates to ensure an upper bound for the excited-state energy. A density functional theory on the basis of this variational principle has been formulated [71, 72, 73]. Since the exact lower eigenstates are not known, however, the use of this formalism is restricted, in practice, to the lowest eigenstate of each symmetry class (where orthogonality to the lower states is ensured by symmetry). A general density-functional formalism, applicable to an arbitrary single excited state is not available.

In this section we shall develop a density-functional formalism for ensembles that allows us to calculate arbitrary excitation energies in principle exactly. The formalism can be viewed as a generalization of Slater's transition state method [74]. In section 3.1, we therefore briefly review the Slater transition state. In the following section, 3.2, a Rayleigh-Ritz principle for ensembles is discussed. This variational principle provides the basis for the excited-state density functional theory to be developed in section 3.3.

3.1 Slater's Transition State

In the Hartree-Fock approach the wave function of an interacting N-electron system is approximated by a Slater determinant. Variation of the total energy with respect to the spin orbitals leads to the equation:

$$\begin{aligned} \left(-\frac{\nabla^2}{2} + v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \right) \varphi_{j\sigma}(\mathbf{r}) &= \int \frac{n_\sigma(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \varphi_{j\sigma}(\mathbf{r}') d^3\mathbf{r}' \\ &= \varepsilon_{j\sigma} \varphi_{j\sigma}(\mathbf{r}) \quad , \quad \sigma = \uparrow\downarrow \end{aligned} \quad (59)$$

with the density matrix

$$n_\sigma(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^{N_\sigma} \varphi_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \quad , \quad N = N_\uparrow + N_\downarrow \quad (60)$$

and the density

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}, \mathbf{r}) + n_\downarrow(\mathbf{r}, \mathbf{r}). \quad (61)$$

Any set of orbitals $\{\varphi_{j\sigma}\}$ that satisfies these equations makes the total energy stationary.

In an ordinary **ground-state** HF calculation, eqs. (59), (60), (61) are solved self-consistently in such a way that, in each iterative step, the N orbitals with **lowest** energies $\varepsilon_{j\sigma}$ are inserted in (60). One is, however, not restricted to this choice of orbitals. If, in each iterative step, one choses e.g. the $N - 1$ lowest orbitals plus the $N + 1$ st state or, more generally,

$$n_\sigma(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^{\infty} f_{j\sigma} \varphi_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \quad (62)$$

with a set of given occupation numbers $f_{j\sigma} = 0$ or 1 , and if the procedure converges (for this given set of occupation numbers) one has obtained another self-consistent solution of eqs. (59), (60), (61) in addition to the ground-state solution. Since the total energy is stationary at this second Slater determinant as well, one has found with this procedure a determinantal approximation for an excited state of the N -particle system.

To simplify the notation, orbitals φ_q and orbital energies ε_q as well as the corresponding occupation numbers f_q will from now on be characterized by one single positive integer q which counts both the orbital quantum numbers and the spin index. The numbering is chosen in such a way, that

$$\varepsilon_1 \leq \varepsilon_2 \leq \varepsilon_3 \leq \dots \quad (63)$$

With this notation, the ground-state HF solution is obtained from eqs. (59), (61), (62) with the vector of occupation numbers

$$\vec{f}_{gs} = \underbrace{(1, 1, \dots, 1)}_N, 0, \dots \quad (64)$$

By contrast, a “particle-hole excitation from orbital q to p ” is obtained with the occupation numbers

$$\vec{f}_{pq} = \underbrace{(1, 1, \dots, 1, 0, 1, \dots, 1)}_N, 0, \dots, 0, \overset{q}{1}, \overset{p}{0}, \dots \quad (65)$$

For any fixed vector \vec{f} of occupation numbers, the self-consistent HF energy is given by

$$\begin{aligned} E_{HF}(\vec{f}) &= \sum_{j=1}^{\infty} f_j \int d^3\mathbf{r} \varphi_j^{(\vec{f})*}(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \varphi_j^{(\vec{f})}(\mathbf{r}) \\ &+ \int d^3\mathbf{r} n^{(\vec{f})}(\mathbf{r}) v(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n^{(\vec{f})}(\mathbf{r}) n^{(\vec{f})}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &- \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n_{\uparrow}^{(\vec{f})}(\mathbf{r}, \mathbf{r}') n_{\uparrow}^{(\vec{f})}(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} - \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n_{\downarrow}^{(\vec{f})}(\mathbf{r}, \mathbf{r}') n_{\downarrow}^{(\vec{f})}(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad (66) \end{aligned}$$

where $\varphi_j^{(\vec{f})}$ and $n^{(\vec{f})}$ are the self-consistent solutions of (59), (61), (62) with the given vector \vec{f} . The excitation energy corresponding to a transition from Φ_{gs} to Φ_{pq} with

$$\Phi_{gs} = \frac{1}{\sqrt{N!}} \det(\varphi_1, \dots, \varphi_N), \quad \Phi_{pq} = \frac{1}{\sqrt{N!}} \det(\varphi_1, \dots, \varphi_{q-1}, \varphi_{q+1}, \dots, \varphi_N, \varphi_p) \quad (67)$$

is then given by

$$\Delta E_{pq} = E_{HF}(\vec{f}_{pq}) - E_{HF}(\vec{f}_{gs}). \quad (68)$$

This method of calculating excitation energies has two major disadvantages. First, the ground-state and the excited-state HF wave functions are generally not orthogonal since they are eigenfunctions of different Hamiltonians. Second, **two** self-consistent calculations are required and, what is even worse, the excitation energy (68) is given as a difference of two large numbers.

Since the wave functions are not very useful anyway (because of the non-orthogonality) Slater [74] introduced a clever way of calculating the excitation energy (only the energy, not the wave function) by **one** self-consistent calculation. This method involves the so-called transition state. The basic idea of this method is quite simple. We introduce transition-state occupation numbers \vec{f}_T by

$$\vec{f}_T = \underbrace{(1, 1, \dots, 1, \frac{1}{2}, 1, \dots, 1, 0, \dots, 0, \frac{1}{2}, 0, \dots)}_N. \quad (69)$$

This suggests that we consider the occupation numbers as arbitrary continuous variables $0 \leq f_i \leq 1$. The **self-consistent** HF energy $E_{HF}(\vec{f})$ then becomes a function of these continuous variables. Setting

$$\delta \vec{f} = (0, \dots, 0, \frac{1}{2}, 0, \dots, 0, -\frac{1}{2}, 0, \dots) \quad (70)$$

we can expand the ground-state energy as

$$E_{HF}(\vec{f}_{gs}) = E_{HF}(\vec{f}_T + \delta \vec{f}) = E_{HF}(\vec{f}_T) + \frac{\partial E_{HF}}{\partial f_q} \Big|_{\vec{f}_T} \underbrace{\delta f_q}_{\frac{1}{2}} + \frac{\partial E_{HF}}{\partial f_p} \Big|_{\vec{f}_T} \underbrace{\delta f_p}_{-\frac{1}{2}} + \dots \quad (71)$$

and similarly the excited-state energy as

$$E_{HF}(\vec{f}_{pq}) = E_{HF}(\vec{f}_T - \delta \vec{f}) = E_{HF}(\vec{f}_T) - \frac{\partial E_{HF}}{\partial f_q} \Big|_{\vec{f}_T} \delta f_q - \frac{\partial E_{HF}}{\partial f_p} \Big|_{\vec{f}_T} \delta f_p + \dots \quad (72)$$

Subtraction of the two equations (71) and (72) leads to a cancellation of the second-order terms in $\delta \vec{f}$ and one obtains

$$\Delta E_{pq} = E_{HF}(\vec{f}_{pq}) - E_{HF}(\vec{f}_{gs}) = \frac{\partial E_{HF}}{\partial f_p} \Big|_{\vec{f}_T} - \frac{\partial E_{HF}}{\partial f_q} \Big|_{\vec{f}_T} + O(\delta f^3). \quad (73)$$

Neglecting the very small terms of order δf^3 and using the identity

$$\frac{\partial E_{HF}(f_1, f_2, \dots)}{\partial f_j} \Big|_{\vec{f}} = \varepsilon_j(\vec{f}) \quad (74)$$

which was first derived by Slater [74] and later extended within the framework of density functional theory by Janak [75], we arrive at

$$\Delta E_{pq} = \varepsilon_p(\vec{f}_T) - \varepsilon_q(\vec{f}_T) \quad (75)$$

where $\varepsilon_p(\vec{f}_T)$ and $\varepsilon_q(\vec{f}_T)$ are the self-consistent HF single-particle energies obtained with the transition state occupation \vec{f}_T .

The obvious advantage of this method is that it requires only **one** self-consistent solution of the HF eqs. (59), (61), (62) for the calculation of an excitation energy.

Using (62) and (69) the transition-state density is

$$n_T(\mathbf{r}) = \sum_{\substack{j=1 \\ j \neq q}}^N |\varphi_j(\mathbf{r})|^2 + \frac{1}{2} |\varphi_p(\mathbf{r})|^2 + \frac{1}{2} |\varphi_q(\mathbf{r})|^2. \quad (76)$$

One has to emphasize that n_T **cannot** be derived from a single Slater determinant. One rather needs an ensemble corresponding to the density-matrix

$$\hat{D} = \frac{1}{2} |\Phi_{gs}\rangle \langle \Phi_{gs}| + \frac{1}{2} |\Phi_{pq}\rangle \langle \Phi_{pq}|. \quad (77)$$

The ensemble density then reproduces the transition-state density:

$$\begin{aligned} tr\{\hat{D}\hat{n}(\mathbf{r})\} &= \frac{1}{2} \langle \Phi_{gs} | \hat{n}(\mathbf{r}) | \Phi_{gs} \rangle + \frac{1}{2} \langle \Phi_{pq} | \hat{n}(\mathbf{r}) | \Phi_{pq} \rangle \\ &= \frac{1}{2} \sum_{j=1}^N |\varphi_j(\mathbf{r})|^2 + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq q}}^N |\varphi_j(\mathbf{r})|^2 + \frac{1}{2} |\varphi_p(\mathbf{r})|^2 = n_T(\mathbf{r}). \end{aligned} \quad (78)$$

In the same way as the traditional density functional formalism for the ground state goes beyond HF by the inclusion of correlation effects, the density functional theory for excited states to be developed below goes beyond the HF calculation of excitation energies described in the present section. The fact that the Slater transition “state” represents an ensemble (and not a pure state) was the motivation to formulate a density functional theory for ensembles. The basis of this formalism is a Rayleigh-Ritz principle for ensembles.

3.2 Rayleigh-Ritz Variational Principle for Ensembles

To keep things as simple as possible, we consider only a two-state ensemble described by the density matrix

$$\hat{D} = \lambda_1 |1\rangle \langle 1| + \lambda_2 |2\rangle \langle 2| \quad (79)$$

where $|1\rangle$, $|2\rangle$ are the exact ground state and the exact first excited state, respectively, of some Hamiltonian \hat{H} :

$$\hat{H}|1\rangle = E_1|1\rangle \quad (80)$$

$$\hat{H}|2\rangle = E_2|2\rangle. \quad (81)$$

For simplicity we further assume these eigenstates to be non-degenerate. This restriction as well as the limitation to a two-state ensemble is by no means essential. The general case of an M-state ensemble including degeneracies is treated in [76].

The ensemble energy associated with \hat{D} is the weighted sum of the ground-state energy and the first excited-state energy:

$$\mathcal{E} = tr\{\hat{D}\hat{H}\} = \lambda_1 E_1 + \lambda_2 E_2. \quad (82)$$

Likewise, the ensemble density is

$$n(\mathbf{r}) = tr\{\hat{D}\hat{n}(\mathbf{r})\} = \lambda_1 n_1(\mathbf{r}) + \lambda_2 n_2(\mathbf{r}) \quad (83)$$

where $n_1(\mathbf{r})$ and $n_2(\mathbf{r})$ are the densities of the ground state and the first excited state, respectively.

With these preliminaries the variational statement can be formulated as follows: If the weights λ_1, λ_2 satisfy the inequality

$$\lambda_1 \geq \lambda_2 \geq 0 \quad (84)$$

(i.e. if the weight of the ground state is greater than or equal to the weight of the first excited state) then the following inequality is satisfied for any pair of orthonormal, but otherwise arbitrary trial functions Φ_1 and Φ_2 :

$$\lambda_1 \langle \Phi_1 | \hat{H} | \Phi_1 \rangle + \lambda_2 \langle \Phi_2 | \hat{H} | \Phi_2 \rangle \geq \lambda_1 E_1 + \lambda_2 E_2 = \mathcal{E} . \quad (85)$$

For $\lambda_1 \neq \lambda_2$ the equality sign holds if and only if the trial functions Φ_1, Φ_2 are equal to the exact ground state and the exact first excited state, respectively:

$$|\Phi_1\rangle = |1\rangle, |\Phi_2\rangle = |2\rangle . \quad (86)$$

If the weights happen to be equal then the equality sign holds if and only if the trial functions lie in the subspace spanned by the exact eigenfunctions

$$|\Phi_1\rangle, |\Phi_2\rangle \in \langle\langle |1\rangle, |2\rangle \rangle\rangle . \quad (87)$$

The proof of this theorem [76] follows the proof of the traditional Rayleigh-Ritz principle by expansion of the trial functions in the complete set of eigenfunctions of \hat{H} .

3.3 Density Functional Theory for Ensembles

We now consider a many-particle system characterized by the Hamiltonian (1) with fixed particle number N . Requiring the ensemble density (83) to be normalized to N ,

$$N = \int d^3\mathbf{r} n(\mathbf{r}) = \lambda_1 \int d^3\mathbf{r} n_1(\mathbf{r}) + \lambda_2 \int d^3\mathbf{r} n_2(\mathbf{r}) = \lambda_1 N + \lambda_2 N , \quad (88)$$

we obtain

$$\lambda_1 = 1 - \lambda_2 , \quad (89)$$

i.e. the ensemble is characterized by **one** parameter $\lambda \equiv \lambda_2$ only.

The density matrix, ensemble energy and ensemble density then read

$$\hat{D}(\lambda) = (1 - \lambda) |1\rangle \langle 1| + \lambda |2\rangle \langle 2| \quad (90)$$

$$\mathcal{E}(\lambda) = (1 - \lambda) E_1 + \lambda E_2 \quad (91)$$

$$n^{(\lambda)}(\mathbf{r}) = (1 - \lambda) n_1(\mathbf{r}) + \lambda n_2(\mathbf{r}) \quad (92)$$

where

$$0 \leq \lambda \leq \frac{1}{2} \quad (93)$$

must be satisfied to ensure the condition (84) for the validity of the variational principle. Note that for $\lambda = 0$ the usual ground-state density functional formalism is recovered, while the case $\lambda = \frac{1}{2}$ leads to the equi-ensemble density functional formalism first developed by Theophilou [77].

By virtue of eq. (91) we have two options to calculate the excitation energy:

$$E_2 - E_1 = \frac{1}{\lambda} (\mathcal{E}(\lambda) - \mathcal{E}(0)) \quad (94)$$

and

$$E_2 - E_1 = \frac{d}{d\lambda} \mathcal{E}(\lambda). \quad (95)$$

To establish a HK theorem for ensembles, we compare two ensemble densities $n(\mathbf{r})$ and $n'(\mathbf{r})$ which, for a fixed value of λ , are generated by the eigenfunctions $\{|1\rangle, |2\rangle\}$ and $\{|1'\rangle, |2'\rangle\}$ of two potentials $v(\mathbf{r})$ and $v'(\mathbf{r})$, respectively. Following the standard HK argument and using the variational principle stated in the last section, one can easily prove [78] a HK theorem for the ensemble density:

$$v(\mathbf{r}) \neq v'(\mathbf{r}) + \text{const} \implies n(\mathbf{r}) \neq n'(\mathbf{r}). \quad (96)$$

Thus, for given λ , the ensemble density uniquely determines the external potential, its eigenstates and therefore the density matrix, $\hat{D} = \hat{D}[n]$. As a consequence, any ensemble expectation value is a functional of the ensemble density.

Now consider a particular system with external potential $v_0(\mathbf{r})$, ensemble density $n_0(\mathbf{r})$ and ensemble energy \mathcal{E}_0 . Then the total energy functional

$$E_{v_0}^{(\lambda)}[n] = F^{(\lambda)}[n] + \int d^3\mathbf{r} n(\mathbf{r}) v_0(\mathbf{r}) \quad (97)$$

with

$$F^{(\lambda)}[n] = \text{tr}\{\hat{D}[n](\hat{T} + \hat{U})\} \quad (98)$$

has the variational properties

$$\begin{aligned} E_{v_0}^{(\lambda)}[n] &> \mathcal{E}_0 && \text{if } n(\mathbf{r}) \neq n_0(\mathbf{r}) \\ E_{v_0}^{(\lambda)}[n] &= \mathcal{E}_0 && \text{if } n(\mathbf{r}) = n_0(\mathbf{r}) \end{aligned} \quad (99)$$

Thus the exact ensemble energy and density can be calculated by minimizing (97).

Similar to the ground-state formalism, the HK principle can be exploited to derive a KS scheme for ensembles stating that the exact ensemble density of the interacting system can be calculated as the ensemble density obtained from the ground state Slater determinant $|1_s\rangle$ and the first excited state Slater determinant $|2_s\rangle$ of a non-interacting KS system. The resulting KS equations

$$\left(-\frac{\nabla^2}{2} + v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}^{(\lambda)}[n](\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad (100)$$

$$\begin{aligned} n(\mathbf{r}) &= (1 - \lambda) \langle 1_s | \hat{n}(\mathbf{r}) | 1_s \rangle + \lambda \langle 2_s | \hat{n}(\mathbf{r}) | 2_s \rangle \\ &= \sum_{j=1}^{N-1} |\varphi_j(\mathbf{r})|^2 + (1 - \lambda) |\varphi_N(\mathbf{r})|^2 + \lambda |\varphi_{N+1}(\mathbf{r})|^2 \end{aligned} \quad (101)$$

have to be solved self-consistently for each fixed value of λ . As usual, the xc-potential is given by

$$v_{xc}^{(\lambda)}[n](\mathbf{r}) = \frac{\delta E_{xc}^{(\lambda)}[n]}{\delta n(\mathbf{r})} \quad (102)$$

where the xc-energy functional is formally defined as

$$E_{xc}^{(\lambda)}[n] = F^{(\lambda)}[n] - T_s^{(\lambda)}[n] - \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (103)$$

In terms of the KS eigenvalues ε_j the total ensemble energy is given by

$$\begin{aligned} \mathcal{E}(\lambda) &= \sum_{j=1}^{N-1} \varepsilon_j(\lambda) + (1 - \lambda)\varepsilon_N(\lambda) + \lambda\varepsilon_{N+1}(\lambda) + E_{xc}^{(\lambda)}[n^{(\lambda)}] - \\ &- \frac{1}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n^{(\lambda)}(\mathbf{r})n^{(\lambda)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - \int d^3\mathbf{r} n^{(\lambda)}(\mathbf{r}) v_{xc}^{(\lambda)}[n^{(\lambda)}](\mathbf{r}). \end{aligned} \quad (104)$$

For $\lambda \rightarrow 0$ this result reduces to the ground-state-energy expression (41). From eq. (95) one finds for the excitation energy

$$E_2 - E_1 = \frac{d}{d\lambda} \mathcal{E}(\lambda) = \varepsilon_{N+1}(\lambda) - \varepsilon_N(\lambda) + \left. \frac{\partial E_{xc}^{(\lambda)}[n]}{\partial \lambda} \right|_{n=n^{(\lambda)}}. \quad (105)$$

Here $\left. \frac{\partial E_{xc}^{(\lambda)}[n]}{\partial \lambda} \right|_{n=n^{(\lambda)}}$ denotes the derivative with respect to λ of the **functional only** (i.e. the derivative of $n^{(\lambda)}$ is not to be taken). Since the KS eigenvalues are smaller than the ensemble energies, the excitation energy $E_2 - E_1$ can be computed more accurately from (105) than from (94).

Eq.(105) is the central result of the density functional theory for ensembles. It provides a formally exact representation of the excitation energy $E_2 - E_1$ and, therefore, can be viewed as an “exactification” of the transition-state formula (75). Eq.(105) is valid for any value of λ in the interval $[0, \frac{1}{2}]$. In the limit $\lambda \rightarrow 0$, eq.(105) leads to a new formula for the band gap in insulators

$$E_{gap} = \varepsilon_C - \varepsilon_V + \lim_{\lambda \rightarrow 0} \left. \frac{\partial E_{xc}^\lambda}{\partial \lambda} \right|_{n=n_{gs}} \quad (106)$$

which can be used as an alternative to eq.(50).

As in the ground-state case, practical calculations require explicit approximations for the xc functional $E_{xc}^{(\lambda)}[n]$. For the equi-ensemble, Kohn [79] proposed an approximation by identifying the xc energy functional of an M-state ensemble with the (available) LDA of a thermal ensemble with entropy $S = k_B \ln M$. This approximation has been successfully applied in a calculation of the excitation spectrum of the He atom [80].

4 DENSITY FUNCTIONAL THEORY FOR TIME-DEPENDENT SYSTEMS

The first steps towards a time-dependent KS scheme were taken by Peuckert [81] and by Zangwill and Soven [82]. These authors treated the linear density response of rare-gas atoms to a time-dependent external potential as the response of non-interacting electrons to an effective time-dependent potential. In analogy to stationary KS theory, this effective potential was assumed to contain an exchange-correlation part, $v_{xc}(\mathbf{r}t)$, in addition to the time-dependent external and Hartree terms:

$$v_s(\mathbf{r}t) = v(\mathbf{r}t) + \int \frac{n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}(\mathbf{r}t) \quad (107)$$

Peuckert suggested an iterative scheme for the calculation of v_{xc} , while Zangwill and Soven adopted the functional form of the static exchange-correlation potential in LDA, i.e.

$$v_{xc}(\mathbf{r}t) = \left. \frac{\partial e_{xc}^{hom}(n)}{\partial n} \right|_{n=n(\mathbf{r}t)}. \quad (108)$$

This approximation can be expected to be good only if the time-dependence of $n(\mathbf{r}t)$ is sufficiently slow. In practice, however, it gave quite good results even for the case of rather rapid time-dependence.

The approach of Zangwill and Soven is valid **under the assumption** that a time-dependent KS theorem exists. Significant steps towards a rigorous foundation of time-dependent density functional theory were taken by Deb and Ghosh [83] - [86] and by Bartolotti [87] - [90] who formulated and explored HK and KS type theorems for the time-dependent density. Each of these derivations, however, was restricted to a rather narrow set of allowable time-dependent potentials (to potentials periodic in time in the theorems of Deb and Ghosh, and to adiabatic processes in the work of Bartolotti). A general formulation covering essentially all time-dependent potentials of interest was given by Runge and Gross [91]. A detailed description of the time-dependent density functional formalism will be presented in section 4.1. The central result is a set of time-dependent KS equations which are structurally similar to the time-dependent Hartree equations but include (in principle exactly) all many-body correlations through a **local** time-dependent exchange-correlation potential.

To date, most applications of the formalism fall in the regime of linear response. The linear-response limit of time-dependent density functional theory will be discussed in section 4.2.

4.1 Basic Theorems

In this section we deal with many-electron systems moving in an explicitly time-dependent potential

$$\hat{V}(t) = \sum_{\sigma} \int d^3\mathbf{r} v(\mathbf{r}, t) \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r}) \hat{\psi}_{\sigma}(\mathbf{r}). \quad (109)$$

The total Hamiltonian is given by

$$\hat{H}(t) = \hat{T} + \hat{U} + \hat{V}(t) \quad (110)$$

where \hat{T} is the kinetic energy (2) of the electrons and \hat{U} is the mutual Coulomb interaction (4). The number of electrons, N , is fixed.

Ordinary time-independent density functional theory is based on the existence of an exact mapping between densities and external potentials. In the ground-state formalism, the existence proof relies on the Rayleigh-Ritz minimum principle for the energy. Straightforward extension to the time-dependent domain is not possible since a **minimum** principle is not available in this case. The existence proof for a 1-1 mapping between time-dependent potentials and time-dependent densities, first given by Runge and Gross [91], is somewhat more involved and will briefly be indicated below. Starting from the time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \Phi(t) = \hat{H}(t) \Phi(t) \quad (111)$$

we shall investigate the densities $n(\mathbf{r}t)$ of electronic systems evolving from a **fixed** initial (many-particle) state

$$\Phi(t_0) = \Phi_0 \quad (112)$$

under the influence of different external potentials $v(\mathbf{r}t)$. For each fixed initial state Φ_0 , formal solution of the Schrödinger equation (111) defines a map

$$\mathcal{A} : v(\mathbf{r}t) \longrightarrow \Phi(t) \quad (113)$$

between the external potentials and the corresponding time-dependent many-particle wave functions and a second map

$$\mathcal{B} : \Phi(t) \longrightarrow n(\mathbf{r}t) = \langle \Phi(t) | \hat{n}(\mathbf{r}) | \Phi(t) \rangle \quad (114)$$

between the many-particle wave functions and the time-dependent densities. Once again, the aim is to prove invertibility of the complete map

$$\mathcal{G} : v(\mathbf{r}t) \longrightarrow n(\mathbf{r}t) . \quad (115)$$

In the following we shall demonstrate that if the potentials $v(\mathbf{r}t)$ are required to be expandable into a Taylor series with respect to the time coordinate around the initial time t_0 , then the map \mathcal{G} is indeed invertible up to within an additive, merely time-dependent function in the potential. In other words, two densities $n(\mathbf{r}t)$ and $n'(\mathbf{r}t)$ evolving from a common initial state Φ_0 under the influence of the potentials $v(\mathbf{r}t)$ and $v'(\mathbf{r}t)$ are always different provided that the potentials differ by more than a purely time-dependent function

$$v(\mathbf{r}t) \neq v'(\mathbf{r}t) + c(t) . \quad (116)$$

Using the condition that the potentials v and v' can be expanded into a Taylor series,

$$v(\mathbf{r}t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_k(\mathbf{r})(t - t_0)^k \quad (117)$$

$$v'(\mathbf{r}t) = \sum_{k=0}^{\infty} \frac{1}{k!} v'_k(\mathbf{r})(t - t_0)^k , \quad (118)$$

eq. (116) is equivalent to the statement that for the expansion coefficients $v_k(\mathbf{r})$ and $v'_k(\mathbf{r})$ there exists a smallest integer $k \geq 0$ such that

$$v_k(\mathbf{r}) - v'_k(\mathbf{r}) = \frac{\partial^k}{\partial t^k} (v(\mathbf{r}t) - v'(\mathbf{r}t)) \Big|_{t=t_0} \neq \text{const} . \quad (119)$$

To demonstrate the 1-1 correspondence we prove in a first step that the current densities

$$\mathbf{j}(\mathbf{r}t) = \langle \Phi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Phi(t) \rangle \quad (120)$$

and

$$\mathbf{j}'(\mathbf{r}t) = \langle \Phi'(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Phi'(t) \rangle \quad (121)$$

are different for different potentials v and v' . Here,

$$\hat{\mathbf{j}}(\mathbf{r}) = -\frac{1}{2i} \sum_{\sigma} \left(\hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})(\nabla \hat{\psi}_{\sigma}(\mathbf{r})) - (\nabla \hat{\psi}_{\sigma}^{\dagger}(\mathbf{r})) \hat{\psi}_{\sigma}(\mathbf{r}) \right) \quad (122)$$

is the usual paramagnetic current density operator. In a second step we shall show that the densities n and n' are different.

Using the quantum mechanical equation of motion for an operator $\hat{O}(t)$

$$\frac{\partial}{\partial t} \langle \Phi(t) | \hat{O}(t) | \Phi(t) \rangle = \langle \Phi(t) | \frac{\partial \hat{O}}{\partial t} - i[\hat{O}(t), \hat{H}(t)] | \Phi(t) \rangle \quad (123)$$

we obtain for the current densities

$$\frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}t) = \frac{\partial}{\partial t} \langle \Phi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Phi(t) \rangle = -i \langle \Phi(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Phi(t) \rangle \quad (124)$$

$$\frac{\partial}{\partial t} \mathbf{j}'(\mathbf{r}t) = \frac{\partial}{\partial t} \langle \Phi'(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Phi'(t) \rangle = -i \langle \Phi'(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}'(t)] | \Phi'(t) \rangle . \quad (125)$$

Since Φ and Φ' evolve from the same initial state

$$\Phi(t_0) = \Phi'(t_0) = \Phi_0 \quad (126)$$

we can write

$$\begin{aligned} \frac{\partial}{\partial t} (\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)) \Big|_{t=t_0} &= -i \langle \Phi_0 | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Phi_0 \rangle \\ &= n_0(\mathbf{r}) \nabla (v(\mathbf{r}t_0) - v'(\mathbf{r}t_0)) \end{aligned} \quad (127)$$

with the initial density

$$n_0(\mathbf{r}) = \langle \Phi_0 | \hat{n}(\mathbf{r}) | \Phi_0 \rangle . \quad (128)$$

If the condition (119) is satisfied for $k = 0$ the right hand side of (127) can not vanish identically and \mathbf{j} and \mathbf{j}' will become different infinitesimally later than t_0 . If (119) holds for some finite $k \geq 0$ we use eq. (123) ($k + 1$) times and obtain after some algebra

$$\left(\frac{\partial}{\partial t} \right)^{k+1} (\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)) \Big|_{t=t_0} = n_0(\mathbf{r}) \nabla w_k(\mathbf{r}) \neq 0 \quad (129)$$

with

$$w_k(\mathbf{r}) = \left(\frac{\partial}{\partial t} \right)^k (v(\mathbf{r}t) - v'(\mathbf{r}t)) \Big|_{t=t_0} . \quad (130)$$

Once again, we conclude from (119) that

$$\mathbf{j}(\mathbf{r}t) \neq \mathbf{j}'(\mathbf{r}t) \quad (131)$$

provided that (116) holds for v and v' . To prove the corresponding statement for the densities we use the continuity equation

$$\frac{\partial}{\partial t} (n(\mathbf{r}t) - n'(\mathbf{r}t)) = -\nabla \cdot (\mathbf{j}(\mathbf{r}t) - \mathbf{j}'(\mathbf{r}t)) \quad (132)$$

and calculate the $(k + 1)$ st time-derivative at $t = t_0$:

$$\left(\frac{\partial}{\partial t} \right)^{k+2} (n(\mathbf{r}t) - n'(\mathbf{r}t)) \Big|_{t=t_0} = -\nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) . \quad (133)$$

In order to prove that the densities $n(\mathbf{r}t)$ and $n'(\mathbf{r}t)$ will become different infinitesimally later than t_0 , we have to demonstrate that the right hand side of eq. (133) cannot vanish identically. This is done by reductio ad absurdum: Assume

$$\nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) \equiv 0 \quad (134)$$

and evaluate the integral

$$\begin{aligned} & \int d^3\mathbf{r} n_0(\mathbf{r}) (\nabla w_k(\mathbf{r}))^2 = \\ & = - \int d^3\mathbf{r} w_k(\mathbf{r}) \nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) + \oint d\mathbf{S} (n_0(\mathbf{r}) w_k(\mathbf{r}) \nabla w_k(\mathbf{r})) \end{aligned} \quad (135)$$

where we have used Green's theorem. The first integral on the right hand side of (135) vanishes by assumption. For physically reasonable potentials (i.e. potentials arising from normalizable external charge densities), the surface integral vanishes as well. Since the integrand on the left hand side is non-negative one concludes that

$$n_0(\mathbf{r}) (\nabla w_k(\mathbf{r}))^2 \equiv 0 \quad (136)$$

in contradiction to $w_k(\mathbf{r}) \neq \text{const.}$ This completes the proof of the theorem.

Having established the existence of the inverse map

$$\mathcal{G}^{-1} : n(\mathbf{r}t) \longrightarrow v(\mathbf{r}t) + c(t) , \quad (137)$$

subsequent application of the map \mathcal{A} tells us that the many-particle wave function is a functional of the time-dependent density, unique up to within a purely time-dependent phase $\alpha(t)$

$$\Phi(t) = e^{-i\alpha(t)} \Psi[n](t) . \quad (138)$$

The ambiguity in the phase, $\alpha(t)$, and the ambiguity in the potential, $c(t)$ are related via

$$\dot{\alpha}(t) = Nc(t) \quad (139)$$

which is readily verified by insertion in the Schrödinger equation. Therefore the expectation value of any quantum mechanical operator \hat{Q} is a **unique** functional of the density

$$Q[n](t) = \langle \Psi[n](t) | \hat{Q}(t) | \Psi[n](t) \rangle . \quad (140)$$

The ambiguity in the phase cancels out.

Furthermore, as a consequence of (138) and (139), the quantum mechanical action integral

$$A[n] = \int_{t_0}^{t_1} dt \langle \Psi[n](t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi[n](t) \rangle \quad (141)$$

is a unique functional of the density, too. Since the quantum mechanical action (as a functional of the wave function) has a stationary point at the exact solution of the Schrödinger equation (111) with the initial condition (112), and since the wave functions are in 1-1 correspondence with the densities, the exact time-dependent density must be a stationary point of the density functional (141), i.e. we can compute the exact density by solving the Euler equation

$$\frac{\delta A[n]}{\delta n(\mathbf{r}t)} = 0 . \quad (142)$$

This variational principle for the time-dependent density allows us to establish a time-dependent KS scheme which reads as follows:

The exact time-dependent density of a system of interacting particles can be calculated as the density

$$n(\mathbf{r}t) = \sum_j \varphi_j^*(\mathbf{r}t) \varphi_j(\mathbf{r}t) \quad (143)$$

of non-interacting particles

$$i\frac{\partial}{\partial t}\varphi_j(\mathbf{r}t) = \left(-\frac{\nabla^2}{2} + v_s[n](\mathbf{r}t)\right)\varphi_j(\mathbf{r}t) \quad (144)$$

moving in the effective, local single-particle potential

$$v_s[n](\mathbf{r}t) = v(\mathbf{r}t) + \int d^3\mathbf{r}' \frac{n(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}t). \quad (145)$$

The proof [91, 5] is analogous to the ground-state case and will not be repeated here.

Once again, the great advantage of the time-dependent KS scheme lies in its computational simplicity compared to other methods such as time-dependent configuration interaction. The time-dependent KS equations have been successfully applied to the semi-classical description of atomic scattering processes [92, 93, 94].

4.2 Frequency-dependent Linear Response

In this section we shall consider the density response of an N-electron system being initially, i.e. at times $t \leq t_0$, in its ground state. In this case, the initial density $n_0(\mathbf{r})$ can be calculated from the ordinary ground-state KS equations

$$\left(-\frac{\nabla^2}{2} + v_0(\mathbf{r}) + \int \frac{n_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}[n_0](\mathbf{r})\right)\varphi_j^{(0)}(\mathbf{r}) = \varepsilon_j\varphi_j^{(0)}(\mathbf{r}) \quad (146)$$

$$n(\mathbf{r}) = \sum_{\text{lowestN}} |\varphi_j^{(0)}(\mathbf{r})|^2. \quad (147)$$

At $t = t_0$ a perturbation is switched on so that the total potential is given by

$$v(\mathbf{r}t) = v_0(\mathbf{r}) + v_1(\mathbf{r}t) \quad (148)$$

$$v_1(\mathbf{r}t) = 0 \quad \text{for } t \leq t_0. \quad (149)$$

The objective is to calculate the linear density response $n_1(\mathbf{r}t)$ to the perturbation $v_1(\mathbf{r}t)$. Conventionally, n_1 is computed from the full linear response function χ as

$$n_1(\mathbf{r}t) = \int d^3\mathbf{r}' \int_{t_0}^{\infty} dt' \chi(\mathbf{r}t, \mathbf{r}'t') v_1(\mathbf{r}'t'). \quad (150)$$

Since the time-dependent KS equations (143) - (145) provide a formally exact way of calculating the time-dependent density, we can compute the exact density response $n_1(\mathbf{r}t)$ as the response of the non-interacting KS system

$$n_1(\mathbf{r}t) = \int d^3\mathbf{r}' \int_{t_0}^{\infty} dt' \chi_{KS}(\mathbf{r}t, \mathbf{r}'t') v_s^{(1)}(\mathbf{r}'t') \quad (151)$$

where $v_s^{(1)}$ is the effective time-dependent potential evaluated to **first** order in the perturbing potential, i.e.

$$v_s^{(1)}(\mathbf{r}t) = v_1(\mathbf{r}t) + \int d^3\mathbf{r}' \frac{n_1(\mathbf{r}'t)}{|\mathbf{r} - \mathbf{r}'|} + \int d^3\mathbf{r}' \int dt' f_{xc}(\mathbf{r}t, \mathbf{r}'t') n_1(\mathbf{r}'t). \quad (152)$$

Here the exchange-correlation kernel f_{xc} is given by the functional derivative of v_{xc}

$$f_{xc}(\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta v_{xc}[n](\mathbf{r}t)}{\delta n(\mathbf{r}'t')} \right|_{n=n_0} \quad (153)$$

evaluated at the initial ground-state density n_0 .

While the full response function χ is very hard to calculate, the non-interacting KS response function can be computed fairly easily. In terms of the static initial KS orbitals $\varphi_j^{(0)}$ (eq. (146)), the Fourier transform of $\chi_{KS}(\mathbf{r}t, \mathbf{r}'t')$ with respect to $(t - t')$ can be expressed as

$$\chi_{KS}(\mathbf{r}, \mathbf{r}'; \omega) = \lim_{\delta \rightarrow 0^+} \sum_{k,j} (f_k - f_j) \frac{\varphi_k^{(0)}(\mathbf{r})^* \varphi_j^{(0)}(\mathbf{r}) \varphi_j^{(0)}(\mathbf{r}')^* \varphi_k^{(0)}(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_k) + i\delta} \quad (154)$$

where f_k, f_j are the usual Fermi occupation factors.

Eqs. (151) and (152) constitute the KS equations for the linear density response. They provide a formally exact self-consistent scheme to calculate the density response $n_1(\mathbf{r}t)$.

For practical applications one has to find approximations for the exchange-correlation kernel f_{xc} . To this end, it is useful to express f_{xc} in terms of the full response function χ . An exact representation of f_{xc} is readily obtained by solving eq.(150) for v_1 and inserting the result in eq.(152). Eq.(151) then yields

$$f_{xc}[n_0](\mathbf{r}t, \mathbf{r}'t') = \chi_{KS}^{-1}[n_0](\mathbf{r}t, \mathbf{r}'t') - \chi^{-1}[n_0](\mathbf{r}t, \mathbf{r}'t') - \frac{\delta(t - t')}{|\mathbf{r} - \mathbf{r}'|} \quad (155)$$

where χ_{KS}^{-1} and χ^{-1} stand for the kernels of the corresponding inverse integral operators.

Once again, the most straightforward approximation for f_{xc} is the LDA where the **functional** $f_{xc}[n_0]$ is replaced by the corresponding **function** $f_{xc}^{hom}(n_0)$ of the homogeneous electron gas, evaluated at the initial density $n_0(\mathbf{r})$ of the actual inhomogeneous system:

$$f_{xc}^{LDA}[n_0](\mathbf{r}t, \mathbf{r}'t') := f_{xc}^{hom}(n_0, |\mathbf{r} - \mathbf{r}'|, (t - t')). \quad (156)$$

In the homogeneous case, Fourier transformation with respect to $(\mathbf{r} - \mathbf{r}')$ and $(t - t')$ makes life easier. Eq.(155) then reads

$$f_{xc}^{hom}(n_0, q, \omega) = \frac{1}{\chi_{KS}^{hom}(n_0, q, \omega)} - \frac{1}{\chi^{hom}(n_0, q, \omega)} - \frac{4\pi}{q^2}. \quad (157)$$

In this case, the response function χ_{KS}^{hom} of a non-interacting homogeneous system is of course well-known: χ_{KS}^{hom} is identical with the Lindhard function.

Eq.(157) shows that the response function χ^{hom} of the homogeneous electron gas uniquely determines the xc kernel f_{xc}^{hom} and thus f_{xc}^{LDA} . Unfortunately, χ^{hom} is not known exactly. However, some exact features of χ^{hom} are known. From these, the following exact properties of f_{xc}^{hom} can be deduced:

1. As a consequence of the compressibility sum rule one finds [95]

$$\lim_{q \rightarrow 0} f_{xc}^{hom}(q, \omega = 0) = \frac{d^2}{dn^2}(e_{xc}^{hom}(n)) \equiv f_0(n) \quad (158)$$

where, as before, $e_{xc}^{hom}(n)$ denotes the exchange-correlation energy per volume of the homogeneous electron gas.

2. The third-frequency-moment sum rule leads to [96]

$$\begin{aligned} & \lim_{q \rightarrow 0} f_{xc}^{hom}(q, \omega = \infty) \\ &= -\frac{4}{5} n^{2/3} \frac{d}{dn} \left(\frac{e_{xc}^{hom}(n)}{n^{5/3}} \right) + 6n^{1/3} \frac{d}{dn} \left(\frac{e_{xc}^{hom}(n)}{n^{4/3}} \right) \equiv f_\infty(n). \end{aligned} \quad (159)$$

3. According to the best estimates [97, 26] of e_{xc}^{hom} , the following relation holds for all densities

$$f_0(n) < f_\infty(n) < 0. \quad (160)$$

4. In the static limit ($\omega = 0$), the short-wavelength behavior is given by [98]

$$\lim_{q \rightarrow \infty} f_{xc}^{hom}(q, \omega = 0) = -\frac{4\pi}{q^2}(1 - g(0)) \quad (161)$$

where $g(r)$ denotes the pair correlation function.

5. For frequencies $\omega \neq 0$, the short-wavelength behavior is [99]

$$\lim_{q \rightarrow \infty} f_{xc}^{hom}(q, \omega \neq 0) = -\frac{2}{3} \cdot \frac{4\pi}{q^2}(1 - g(0)). \quad (162)$$

6. $f_{xc}^{hom}(q, \omega)$ is a complex-valued function satisfying the symmetry relations

$$Re f_{xc}^{hom}(q, \omega) = Re f_{xc}^{hom}(q, -\omega) \quad (163)$$

$$Im f_{xc}^{hom}(q, \omega) = -Im f_{xc}^{hom}(q, -\omega). \quad (164)$$

7. $f_{xc}^{hom}(q, \omega)$ is an analytic function of ω in the upper half of the complex ω -plane and approaches a real function $f_\infty(q)$ for $\omega \rightarrow \infty$ [100]. Therefore, the function $f_{xc}^{hom}(q, \omega) - f_\infty(q)$ satisfies standard Kramers-Kronig relations:

$$Re f_{xc}^{hom}(q, \omega) - f_\infty(q) = \mathbf{P} \int \frac{d\omega'}{\pi} \frac{Im f_{xc}^{hom}(q, \omega')}{\omega' - \omega} \quad (165)$$

$$Im f_{xc}^{hom}(q, \omega) = -\mathbf{P} \int \frac{d\omega'}{\pi} \frac{Re f_{xc}^{hom}(q, \omega') - f_\infty(q)}{\omega' - \omega}. \quad (166)$$

8. The imaginary part of f_{xc}^{hom} exhibits the high-frequency behavior

$$\lim_{\omega \rightarrow \infty} Im f_{xc}^{hom}(q, \omega) = -\frac{c}{\omega^{3/2}} \quad (167)$$

for any $q < \infty$ [101]. A second-order perturbation expansion [101, 102] of the irreducible polarization propagator leads to the high-density limit

$$c = \frac{23\pi}{15}. \quad (168)$$

9. In the same limit, the real part of f_{xc}^{hom} behaves like [103]

$$\lim_{\omega \rightarrow \infty} Re f_{xc}^{hom}(q, \omega) = f_\infty(q) + \frac{c}{\omega^{3/2}}. \quad (169)$$

Since $c > 0$, the infinite-frequency value f_∞ is approached from above. This implies, in view of the relation (160), that $Re f_{xc}^{hom}(q = 0, \omega)$ cannot grow monotonically from f_0 to f_∞ .

The above features of f_{xc}^{hom} are valid for a three-dimensional electron gas. Analogous results have been obtained for the two-dimensional case [101, 104, 105].

The approximation (108) employed by Zangwill and Soven leads, by virtue of eq. (153), to the following approximation for f_{xc} :

$$f_{xc}^{ZS}(\mathbf{r}t, \mathbf{r}'t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}') \frac{d^2 e_{xc}^{hom}(n)}{dn^2} \Big|_{n=n_0(\mathbf{r})}. \quad (170)$$

Comparison with (158) shows, that

$$f_{xc}^{ZS}(\mathbf{r}t, \mathbf{r}'t') = \delta(t - t')\delta(\mathbf{r} - \mathbf{r}') f_{xc}^{hom}(q = 0, \omega = 0) \Big|_{n=n_0(\mathbf{r})}. \quad (171)$$

In other words, Zangwill and Soven employed the static ($\omega = 0$) response of the homogeneous electron gas. Gross and Kohn [5, 103] went beyond this limit by explicitly including the frequency dependence of f_{xc}^{hom} . Taking into account the exact high- and low-frequency limits, Gross and Kohn proposed the following parametrization:

$$Im f_{xc}^{hom}(q = 0, \omega) = \frac{a(n)\omega}{(1 + b(n)\omega^2)^{5/4}} \quad (172)$$

where

$$a(n) = -c(\gamma/c)^{5/3}(f_\infty(n) - f_0(n))^{5/3} \quad (173)$$

$$b(n) = (\gamma/c)^{4/3}(f_\infty(n) - f_0(n))^{4/3} \quad (174)$$

$$\gamma = \frac{(\Gamma(1/4))^2}{4\sqrt{2\pi}}. \quad (175)$$

f_0 , f_∞ and c are given by eqs. (158), (159), and (168), respectively. Using the Kramers-Kronig relation (165), the real part can be expressed as

$$\begin{aligned} & Re f_{xc}^{hom}(q = 0, \omega) \\ &= f_\infty + \frac{a}{\pi s^2} \sqrt{\frac{8}{b}} \left[2E\left(\frac{1}{\sqrt{2}}\right) - \frac{1+s}{2} \Pi\left(\frac{1-s}{2}, \frac{1}{\sqrt{2}}\right) \right. \\ &\quad \left. - \frac{1-s}{2} \Pi\left(\frac{1+s}{2}, \frac{1}{\sqrt{2}}\right) \right], \quad s^2 = 1 + b\omega^2. \end{aligned} \quad (176)$$

E and Π are complete elliptic integrals of the second and third kind in the standard notation of Byrd and Friedman [106].

Figs.1 and 2 show the real and imaginary part of f_{xc}^{hom} as calculated from (172) and (176). The functions are plotted for the two density values corresponding to $r_s = 2$ and $r_s = 4$. For the lower density value ($r_s = 4$), a considerable frequency-dependence is found. The dependence on ω becomes less pronounced for higher densities. In the extreme high-density limit, the difference between f_0 and f_∞ tends to zero. One finds the exact result

$$f_\infty - f_0 \sim r_s^2 \quad \text{for } r_s \rightarrow 0. \quad (177)$$

At the same time, the depth of the minimum of $Im f_{xc}^{hom}$ decreases, again proportional to r_s^2 .

Fig.1. Real part of the parametrization for $f_{xc}^{hom}(q = 0, \omega)$
(from [96])

Fig.2. Imaginary part of the parametrization for
 $f_{xc}^{hom}(q = 0, \omega)$ (from [96])

Fig.3. Total photoabsorption cross section of the Xe atom versus photon energy in the vicinity of the 4d threshold (from [82]). Solid line: self-consistent time-dependent KS calculation; dash-dot line: self-consistent time-dependent Hartree calculation ($f_{xc} \equiv 0$); dashed line: independent particle result (Hartree and exchange-correlation kernels neglected); crosses: experimental data from [121].

We finally mention that an extension of the parametrization (172) to nonvanishing q was given by Dabrowski [107]. A similar interpolation for the exchange-correlation kernel of the 2-dimensional electron gas has been derived by Holas and Singwi [101].

The time dependent KS scheme defined by eqs. (151) and (152) has turned out to be remarkably successful. It has been applied to the photo-response of atoms [82, 108, 109] and molecules [110, 111], metallic [112] - [118] and semiconductor [119] surfaces and, most recently, of bulk semiconductors [120]. As an example for the quality of the results we show, in Fig.3, the photoabsorption cross section of xenon.

5 DENSITY FUNCTIONAL THEORY FOR SUPERCONDUCTORS

The traditional description of conventional superconductors is given by the theory of Bardeen, Cooper and Schrieffer (BCS) [122]. This theory assumes the presence of an **attractive** electron-electron interaction induced by the lattice vibrations (phonons) of a solid. The existence of such an effective attractive interaction was first demonstrated by Fröhlich [123]. This interaction leads to pairing, i.e. to the formation of the so-called Cooper pairs [124]. The ansatz of an antisymmetrized product of pair wave functions is the essence of the BCS model. Optimization of this ansatz via the Rayleigh-Ritz principle leads to the famous BCS gap equation. It is easy to see that the BCS ansatz

for the wave function of superconductors is the analogue of the Hartree wave function for normal systems, i.e. exchange-correlation effects are neglected in the BCS model.

In section 5.1 we shall describe a density functional formalism for superconductors which provides a complete and in principle exact description of the superconducting state of matter. The formalism leads to a gap equation that includes, in addition to the BCS terms, an exchange-correlation contribution. This term needs to be approximated. In section 5.2 we shall develop a many-body perturbation theory for superconductors which, in section 5.3, will be used to calculate an approximation for the xc-part of the total-energy functional. On the basis of this approximation, the xc contribution to the gap equation will be deduced.

5.1 Formalism

We consider superconducting systems described by a grand-canonical Hamiltonian of the following form:

$$\begin{aligned} \hat{H} &= \hat{T} + \hat{U} + \hat{W} + \int (v(\mathbf{r}) - \mu) \hat{n}(\mathbf{r}) d^3\mathbf{r} \\ &- \iint \left(D^*(\mathbf{r}, \mathbf{r}') \hat{\psi}_\uparrow(\mathbf{r}) \hat{\psi}_\downarrow(\mathbf{r}') + D(\mathbf{r}, \mathbf{r}') \hat{\psi}_\downarrow^\dagger(\mathbf{r}') \hat{\psi}_\uparrow^\dagger(\mathbf{r}) \right) d^3\mathbf{r} d^3\mathbf{r}'. \end{aligned} \quad (178)$$

As before, \hat{T} is the kinetic energy and \hat{U} the mutual Coulomb repulsion of the electrons. \hat{W} is a (generally nonlocal) pairing interaction

$$\hat{W} = - \int d^3\mathbf{r} \int d^3\mathbf{r}' \int d^3\mathbf{x} \int d^3\mathbf{x}' \hat{\psi}_\downarrow^\dagger(\mathbf{r}) \hat{\psi}_\uparrow^\dagger(\mathbf{r}') w(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \hat{\psi}_\uparrow(\mathbf{x}) \hat{\psi}_\downarrow(\mathbf{x}'). \quad (179)$$

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

Since the most interesting features of superconducting systems sensitively depend on temperature, we are going to formulate the theory for a thermal ensemble.

The density functional formalism, first proposed by Oliveira, Gross and Kohn (OGK) [125], provides a description of superconductors in terms of two “densities”: the normal density $n(\mathbf{r})$ as usual, and the anomalous density

$$\Delta(\mathbf{r}, \mathbf{r}') = \langle \hat{\psi}_\uparrow(\mathbf{r}) \hat{\psi}_\downarrow(\mathbf{r}') \rangle. \quad (180)$$

The diagonal $\Delta(\mathbf{r}, \mathbf{r})$ can be shown [126] to be identical, in the appropriate limits, with the phenomenological order parameter of the Ginzburg-Landau theory [127].

In analogy to the temperature-dependent version [22] of the traditional HK statement, OGK proved a theorem which guarantees the existence of a 1-1 mapping from the **pair** of potentials $\{v(\mathbf{r}) - \mu, D(\mathbf{r}, \mathbf{r}')\}$ onto the **pair** of equilibrium densities $\{n(\mathbf{r}), \Delta(\mathbf{r}, \mathbf{r}')\}$. This statement can be used to derive a set of self-consistent single-particle “KS” equations that determine, in principle exactly, the densities $n(\mathbf{r})$ and $\Delta(\mathbf{r}, \mathbf{r})$ of the interacting system described by the Hamiltonian (178). At any given inverse temperature $\beta = 1/(k_B T)$ these equations are:

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu \right) u_k(\mathbf{r}) + \int D_s(\mathbf{r}, \mathbf{r}') v_k(\mathbf{r}') d^3\mathbf{r}' = E_k u_k(\mathbf{r}) \quad (181)$$

$$- \left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \mu \right) v_k(\mathbf{r}) + \int D_s^*(\mathbf{r}, \mathbf{r}') u_k(\mathbf{r}') d^3\mathbf{r}' = E_k v_k(\mathbf{r}). \quad (182)$$

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

$$n(\mathbf{r}) = 2 \sum_k \left(|u_k(\mathbf{r})|^2 f_\beta(E_k) + |v_k(\mathbf{r})|^2 f_\beta(-E_k) \right) \quad (183)$$

$$\Delta(\mathbf{r}, \mathbf{r}') = \sum_k \left(v_k^*(\mathbf{r}') u_k(\mathbf{r}) f_\beta(-E_k) - v_k^*(\mathbf{r}) u_k(\mathbf{r}') f_\beta(E_k) \right) \quad (184)$$

where f_β denotes the Fermi distribution

$$f_\beta(E) = \frac{1}{1 + e^{\beta E}}. \quad (185)$$

Eqs.(181) and (182) contain two effective single-particle potentials: the “normal” potential $v_s(\mathbf{r})$ and the effective pair potential $D_s(\mathbf{r}, \mathbf{r}')$. Both are functionals of the normal and the anomalous density:

$$v_s[n, \Delta](\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}^\beta[n, \Delta](\mathbf{r}) \quad (186)$$

$$D_s[n, \Delta](\mathbf{r}, \mathbf{r}') = D(\mathbf{r}, \mathbf{r}') + \iint w(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \Delta(\mathbf{x}, \mathbf{x}') d^3\mathbf{x} d^3\mathbf{x}' + D_{xc}^\beta[n, \Delta](\mathbf{r}, \mathbf{r}'). \quad (187)$$

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

$$v_{xc}^\beta[n, \Delta](\mathbf{r}) = \frac{\delta F_{xc}^\beta[n, \Delta]}{\delta n(\mathbf{r})} \quad (188)$$

$$D_{xc}^\beta[n, \Delta](\mathbf{r}, \mathbf{r}') = -\frac{\delta F_{xc}^\beta[n, \Delta]}{\delta \Delta^*(\mathbf{r}, \mathbf{r}')}. \quad (189)$$

Since v_s and D_s depend on the densities the whole set of equations (181) to (189) has to be solved self-consistently. Eqs. (181), (182) are structurally similar to the Bogoliubov-deGennes equations [128], but - in contrast to the latter - include xc effects in principle exactly. We mention that external vector potentials can be included in the formalism in straightforward fashion [129].

Eqs. (181) - (189) can be decoupled exactly [130] into a set of normal KS equations and a BCS-type gap equation. This is achieved with the ansatz

$$u_k(\mathbf{r}) = u_k \varphi_k(\mathbf{r}), \quad v_k(\mathbf{r}) = v_k \varphi_{-k}^*(\mathbf{r}) \quad (190)$$

where u_k and v_k are complex numbers and the φ_k are solutions of the “normal” KS equation

$$\left(-\frac{\nabla^2}{2} + v_s[n, \Delta](\mathbf{r}) \right) \varphi_k(\mathbf{r}) = \varepsilon_k \varphi_k(\mathbf{r}) \quad (191)$$

with the single-particle potential (186). The index k includes crystal momentum and band index. Insertion of (190) in the Bogoliubov-KS equations (181), (182) leads to the 2×2 eigenvalue problem

$$\begin{pmatrix} (\varepsilon_k - \mu) & D_s(k) \\ D_s^*(k) & -(\varepsilon_k - \mu) \end{pmatrix} \begin{pmatrix} u_k \\ v_k \end{pmatrix} = E_k \begin{pmatrix} u_k \\ v_k \end{pmatrix} \quad (192)$$

where

$$D_s(k) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi_k^*(\mathbf{r}) \varphi_{-k}^*(\mathbf{r}') D_s(\mathbf{r}, \mathbf{r}'). \quad (193)$$

This eigenvalue problem is easily solved:

$$E_k = \pm R_k \quad (194)$$

with

$$R_k = \sqrt{(\varepsilon_k - \mu)^2 + |D_s(k)|^2} \quad (195)$$

$$v_k = \frac{1}{\sqrt{2}} \left[1 - \frac{\varepsilon_k - \mu}{E_k} \right]^{\frac{1}{2}} \quad (196)$$

$$u_k = \frac{1}{\sqrt{2}} \text{sign}(E_k) e^{i\delta_k} \left[1 + \frac{\varepsilon_k - \mu}{E_k} \right]^{\frac{1}{2}} \quad (197)$$

where

$$e^{i\delta_k} = \frac{D_s(k)}{|D_s(k)|}. \quad (198)$$

The densities then read

$$n(\mathbf{r}) = \sum_k \left(1 - \frac{\varepsilon_k - \mu}{R_k} \tanh\left(\frac{\beta}{2} R_k\right) \right) |\varphi_k(\mathbf{r})|^2 \quad (199)$$

and

$$\Delta(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_k \frac{D_s(k)}{R_k} \tanh\left(\frac{\beta}{2} R_k\right) \varphi_k(\mathbf{r}) \varphi_{-k}(\mathbf{r}'). \quad (200)$$

Insertion of (187) into (193) leads to the following integral equation for $D_s(k)$:

$$D_s(k) = D(k) + \frac{1}{2} \sum_{k'} \frac{w(k, k') D_s(k')}{R_{k'}} \tanh\left(\frac{\beta R_{k'}}{2}\right) + D_{xc}[D_s](k) \quad (201)$$

where $D(k)$ and $D_{xc}(k)$ are defined in analogy to eq. (193). $w(k, k')$ is given by

$$\begin{aligned} w(k, k') &= \\ &= \int d^3\mathbf{r} \int d^3\mathbf{r}' \int d^3\mathbf{x} \int d^3\mathbf{x}' \varphi_k^*(\mathbf{r}) \varphi_{-k}^*(\mathbf{r}') w(\mathbf{r}, \mathbf{r}', \mathbf{x}, \mathbf{x}') \varphi_{k'}(\mathbf{x}) \varphi_{-k'}(\mathbf{x}'). \end{aligned} \quad (202)$$

Self-consistent solution of eqs. (181) - (189) is completely equivalent to solution of the cycle (191), (199) - (202).

In practice, one starts with an ordinary KS calculation for the material in question, i.e. one solves (191) with v_s given by

$$v_s[n](\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + v_{xc}[n](\mathbf{r}). \quad (203)$$

From this calculation we obtain single-particle orbitals $\varphi_k(\mathbf{r})$ and single-particle energies ε_k . With these ε_k and with $w(k, k')$, resulting from the $\varphi_k(\mathbf{r})$ via (202), we solve the integral equation (201) for D_s and calculate the densities via eqs. (199), (200). Insertion into (186) then yields a new single-particle potential v_s and we start again with eq. (191). The whole cycle is repeated until self-consistency is achieved.

The separation of the original equations (181) - (189) into a traditional KS equation (191) and a BCS type gap equation (201) is of particular importance because it achieves a separation of energy scales: the gap function $D_s(k)$ is usually three orders of magnitude smaller than characteristic features, such as band gaps, of the normal band structure ε_k . Furthermore, the dependence of the single-particle potential (186)

on Δ is expected to be small, so that a self-consistent solution of the traditional KS scheme (i.e. with the single-particle potential $v_s[n]$ of (203)) will be very close to the result of the full self-consistency cycle (191), (199) - (201).

In the homogeneous limit we have

$$\varphi_k(\mathbf{r}) \sim e^{i\mathbf{k}\mathbf{r}} \quad , \quad \varepsilon_k = \frac{k^2}{2} \quad , \quad (204)$$

and eq. (201) reduces rigorously to the BCS gap equation if D_{xc} is neglected. Thus the traditional BCS model can be viewed as the homogeneous Hartree limit of the density functional theory for superconductors presented here.

In order to go beyond BCS one needs approximations for the functional $D_{xc}[D_s]$. The construction of an approximation for D_{xc} in the homogeneous case will be the objective of the subsequent sections.

5.2 Perturbation Theory for Superconductors

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

$$\hat{H} = \hat{H}_0 + \tilde{W} \quad (205)$$

with

$$\begin{aligned} \hat{H}_0 &= \sum_{\sigma=\uparrow\downarrow} \int d^3\mathbf{r} \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left(-\frac{\nabla^2}{2} + v(\mathbf{r}) - \mu \right) \hat{\psi}_\sigma(\mathbf{r}) \\ &\quad - \int d^3\mathbf{r} \int d^3\mathbf{r}' \left(D^*(\mathbf{r}, \mathbf{r}') \hat{\psi}_\uparrow(\mathbf{r}) \hat{\psi}_\downarrow(\mathbf{r}') + D(\mathbf{r}, \mathbf{r}') \hat{\psi}_\downarrow^\dagger(\mathbf{r}') \hat{\psi}_\uparrow^\dagger(\mathbf{r}) \right) \end{aligned} \quad (206)$$

and

$$\begin{aligned} \tilde{W} &= \hat{U} + \hat{W} \\ &:= \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \int d^3\mathbf{r}_3 \int d^3\mathbf{r}_4 \hat{\psi}_\sigma^\dagger(\mathbf{r}_1) \hat{\psi}_{\sigma'}^\dagger(\mathbf{r}_2) \tilde{w}_{\sigma, \sigma'}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \hat{\psi}_{\sigma'}(\mathbf{r}_3) \hat{\psi}_\sigma(\mathbf{r}_4) . \end{aligned} \quad (207)$$

One has to emphasize that \hat{H}_0 already describes a superconducting system due to the external pair potential $D(\mathbf{r}, \mathbf{r}')$. \hat{H}_0 can be diagonalized by the Bogoliubov-Valatin transformation [131]

$$\hat{\psi}_\uparrow(\mathbf{r}) = \sum_k \left(u_k(\mathbf{r}) \hat{\gamma}_{k\uparrow} - v_k^*(\mathbf{r}) \hat{\gamma}_{k\downarrow}^\dagger \right) \quad (208)$$

$$\hat{\psi}_\downarrow(\mathbf{r}) = \sum_k \left(u_k(\mathbf{r}) \hat{\gamma}_{k\downarrow} + v_k^*(\mathbf{r}) \hat{\gamma}_{k\uparrow}^\dagger \right) \quad (209)$$

with fermionic quasi-particle operators $\hat{\gamma}_{k\uparrow}, \hat{\gamma}_{k\downarrow}$. The $u_k(\mathbf{r}), v_k(\mathbf{r})$ satisfy eigenvalue equations with the same algebraic structure as (181), (182) and can be determined in the same manner.

The diagonalized Hamiltonian reads

$$\hat{H}_0 = \sum_k (\varepsilon_k - \mu - R_k) + \sum_{k, \sigma} R_k \hat{\gamma}_{k, \sigma}^\dagger \hat{\gamma}_{k, \sigma} \quad (210)$$

with ε_k being the eigenvalues of the Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + v(\mathbf{r}) \right) \varphi_k(\mathbf{r}) = \varepsilon_k \varphi_k(\mathbf{r}) \quad (211)$$

and

$$R_k = \sqrt{(\varepsilon_k - \mu)^2 + |D(k)|^2} \quad (212)$$

where

$$D(k) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \varphi_k^*(\mathbf{r}) \varphi_{-k}^*(\mathbf{r}') D(\mathbf{r}, \mathbf{r}') . \quad (213)$$

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

$$n(\mathbf{r}) = \sum_k \left(1 - \frac{\varepsilon_k - \mu}{R_k} \tanh\left(\frac{\beta}{2} R_k\right) \right) |\varphi_k(\mathbf{r})|^2 \quad (214)$$

and

$$\Delta(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \sum_k \frac{D(k)}{R_k} \tanh\left(\frac{\beta}{2} R_k\right) \varphi_k(\mathbf{r}) \varphi_{-k}(\mathbf{r}') . \quad (215)$$

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

$$\hat{N}_\gamma = \sum_{k,\sigma} \hat{\gamma}_{k,\sigma}^\dagger \hat{\gamma}_{k,\sigma} . \quad (216)$$

With the complete set of eigenstates of the non-interacting superconductor described by \hat{H}_0 we are able to construct a perturbation theory in the same fashion as it is usually done for normal-state systems.

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

$$\text{Heisenberg picture : } \hat{O}(\tau)_H = e^{\hat{H}\tau} \hat{O} e^{-\hat{H}\tau} \quad (217)$$

$$\text{interaction picture : } \hat{O}(\tau)_I = e^{\hat{H}_0\tau} \hat{O} e^{-\hat{H}_0\tau} , \quad (218)$$

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

$$\hat{U}(\tau, \tau') = e^{\hat{H}_0\tau} e^{-\hat{H}(\tau-\tau')} e^{-\hat{H}_0\tau} . \quad (219)$$

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

$$\frac{\partial}{\partial \tau} \hat{U}(\tau, \tau') = -\tilde{W}(\tau)_I \hat{U}(\tau, \tau') \quad (220)$$

which can formally be solved

$$\hat{U}(\tau, \tau') = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_{\tau'}^{\tau} d\tau_1 \dots \int_{\tau'}^{\tau} d\tau_n \hat{T} \left(\tilde{W}(\tau_1)_I \dots \tilde{W}(\tau_n)_I \right) . \quad (221)$$

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

$$\hat{T} \left(\hat{A}(\tau) \hat{B}(\tau') \right) = \begin{cases} \hat{A}(\tau) \hat{B}(\tau') & \text{if } \tau > \tau' \\ -\hat{B}(\tau') \hat{A}(\tau) & \text{if } \tau' > \tau \end{cases} \quad (222)$$

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

$$\frac{Z}{Z_0} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta d\tau_1 \dots \int_0^\beta d\tau_n \text{Tr} \left\{ \hat{\rho}_0 \hat{T} \left(\tilde{W}(\tau_1)_I \dots \tilde{W}(\tau_n)_I \right) \right\} \quad (223)$$

where

$$Z_0 = \text{tr}\{e^{-\beta\hat{H}_0}\} \quad (224)$$

is the partition function and

$$\hat{\rho}_0 = \frac{e^{-\beta\hat{H}_0}}{\text{Tr}\{e^{-\beta\hat{H}_0}\}} \quad (225)$$

the statistical density operator of the non-interacting system.

Expressing \tilde{W} in terms of the quasi-particle operators $\hat{\gamma}$ and using the complete set of eigenstates of \hat{H}_0 (and \hat{N}_γ) for the evaluation of the trace we are able to prove Wick's theorem. With the definition of the contraction of two operators $\hat{\alpha}_i, \hat{\alpha}_j$

$$\overline{\alpha_i(\tau_i)_I \alpha_j(\tau_j)_I} := \text{Tr}\{\hat{\rho}_0 \hat{T}(\hat{\alpha}_i(\tau_i)_I \hat{\alpha}_j(\tau_j)_I)\} \quad (226)$$

Wick's theorem reads

$$\begin{aligned} \text{Tr}\{\hat{\rho}_0 \hat{T}(\dots \hat{\psi}_{\sigma_i}(\mathbf{r}_i \tau_i)_I \dots \hat{\psi}_{\sigma_j}^\dagger(\mathbf{r}_j \tau_j)_I \dots)\} = \\ = \sum (\text{all completely contracted terms}) \end{aligned} \quad (227)$$

Note that for our superconducting \hat{H}_0 contractions of the form $\overline{\psi\psi}$ or $\overline{\psi^\dagger\psi^\dagger}$ do **not** vanish as in normal-state perturbation theory. Defining one normal and two anomalous one-particle Green's functions of the non-interacting system

$$G_{\sigma\sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau') := -\overline{\psi_\sigma(\mathbf{r}\tau)_I \psi_{\sigma'}^\dagger(\mathbf{r}'\tau')_I} \quad (228)$$

$$F_{\sigma\sigma'}^{(0)}(\mathbf{r}\tau, \mathbf{r}'\tau') := -\overline{\psi_\sigma(\mathbf{r}\tau)_I \psi_{\sigma'}(\mathbf{r}'\tau')_I} \quad (229)$$

$$F_{\sigma\sigma'}^{(0)\dagger}(\mathbf{r}\tau, \mathbf{r}'\tau') := -\overline{\psi_\sigma^\dagger(\mathbf{r}\tau)_I \psi_{\sigma'}^\dagger(\mathbf{r}'\tau')_I} \quad (230)$$

we are now able to write down the Feynman rules for the diagrammatic evaluation of the expansion (223):

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

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

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

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

2. The interaction is represented by

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

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

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

4. The sum over all coordinates at the vertices has to be taken.

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

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

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

with respect to the central vertical axis.

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

$$\frac{Z}{Z_0} = \exp \left(\sum \text{all connected graphs} \right). \quad (231)$$

In Fig.4 we show all topologically distinct graphs contributing to the free energy of the system up to second order in the interaction.

5.3 Exchange-Correlation Contributions to the Gap Equation

In this section we shall present explicit results for the xc part F_{xc} of the free-energy functional obtained with the diagrammatic methods developed in the last sections. The functional derivative (189) of F_{xc} with respect to the anomalous density then leads to the xc terms in the gap equation (201).

We restrict ourselves to the case of a homogeneous electron gas, i.e. to vanishing external potential $v(\mathbf{r}) \equiv 0$, and translationally invariant pair potentials $D(\mathbf{r}, \mathbf{r}') = D(|\mathbf{r} - \mathbf{r}'|)$. Furthermore, we restrict ourselves to the simplified phonon-induced electron-electron interaction adopted by BCS

Fig.4. All topologically distinct, connected graphs contributing to the partition function up to second order

$$\begin{aligned} & \tilde{w}_{\sigma\sigma'}^{BCS}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \\ &= -\delta_{\sigma, -\sigma'} \int \frac{d^3\mathbf{k}}{(2\pi)^3} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} \int \frac{d^3\mathbf{q}}{(2\pi)^3} V(\mathbf{k}', \mathbf{k}' - \mathbf{q}) e^{i\mathbf{k}'(\mathbf{r}_1 - \mathbf{r}_4)} e^{i\mathbf{k}(\mathbf{r}_2 - \mathbf{r}_3)} e^{i\mathbf{q}(\mathbf{r}_2 - \mathbf{r}_1)} \end{aligned} \quad (232)$$

$$V(\mathbf{k}, \mathbf{k}') = \begin{cases} V & \text{if } |\frac{k^2}{2} - \mu| < \omega_D \text{ and } |\frac{k'^2}{2} - \mu| < \omega_D \\ 0 & \text{otherwise} \end{cases} \quad (233)$$

with ω_D being the Debye frequency. The Coulomb interaction of the electrons is neglected. In principle, the formalism is capable of treating the Coulomb interaction as well but, beginning in second order, some of the diagrams contributing to the partition function are divergent (like for the normal-state homogeneous electron gas). A resummation of these divergent graphs to infinite order would be necessary to obtain finite, physically meaningful results. In normal-state perturbation theory the simplest resummation of this kind is known as random phase approximation (RPA) [65].

Under the conditions stated above there is only one contribution to the xc free energy in first order:

$$\begin{aligned} F_{xc}^{(1)} &= F \left[\right] \\ &= -\mathcal{V} \int \frac{d^3\mathbf{k}_1}{(2\pi)^3} \int \frac{d^3\mathbf{k}_2}{(2\pi)^3} V(-\mathbf{k}_1, -\mathbf{k}_1) \\ &\quad \left(1 - \frac{\varepsilon_{\mathbf{k}_1} - \mu}{R_{\mathbf{k}_1}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}_1}\right) \right) \left(1 - \frac{\varepsilon_{\mathbf{k}_2} - \mu}{R_{\mathbf{k}_2}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}_2}\right) \right) \end{aligned} \quad (234)$$

with \mathcal{V} being the volume of the system.

The term involving the anomalous propagators (229), (230)

also contributes to the free energy. This term leads to the Hartree part of D_s (i.e. to the second term on the right hand side of eq. (187)) and is therefore not included in the **exchange-correlation** part of the free energy.

In real physical systems, ω_D/μ is a small quantity. It therefore is not necessary to evaluate all the 28 second order diagrams listed in Fig.4 but only the dominant ones in ω_D/μ . These dominant contributions then give:

$$\begin{aligned} F_{xc}^{(2)} &= F \left[\right] + F \left[\right] \\ &= -\frac{\mathcal{V}}{(2\pi)^3} \left(n^{(0)} \right)^2 \\ &\quad \int d^3\mathbf{k}_1 V(\mathbf{k}_1, \mathbf{k}_1)^2 \left(\frac{|D(\mathbf{k}_1)|^2}{2R_{\mathbf{k}_1}^3} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}_1}\right) + \frac{(\varepsilon_{\mathbf{k}_1} - \mu)^2}{R_{\mathbf{k}_1}^2} \frac{\frac{\beta}{4}}{\cosh^2\left(\frac{\beta}{2} R_{\mathbf{k}_1}\right)} \right) \end{aligned} \quad (235)$$

with

$$n^{(0)} = \int \frac{d^3\mathbf{k}}{(2\pi)^3} \left(1 - \frac{\varepsilon_{\mathbf{k}} - \mu}{R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2} R_{\mathbf{k}}\right) \right). \quad (236)$$

In order to determine the xc functional D_{xc} in the gap equation (201), the functional derivative of F_{xc} with respect to $\Delta^*(\mathbf{r}, \mathbf{r}')$ needs to be calculated. This calculation is

not straightforward because the perturbative result for F_{xc} given in eqs. (234), (235) represents the xc free energy as a functional of the **potentials**

$$F_{xc} = F_{xc}[\mu, D] \quad (237)$$

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

$$n = n[\mu, D] \quad (238)$$

$$\Delta = \Delta[\mu, D]. \quad (239)$$

The HK theorem then guarantees that these two equations can be inverted, leading to the inverse functionals

$$\mu = \mu[n, \Delta] \quad (240)$$

$$D = D[n, \Delta]. \quad (241)$$

If we knew these functionals then, by insertion into (237), we would have an expression for F_{xc} as a functional of the densities, $F_{xc} = F_{xc}[n, \Delta]$. The inverse functionals (240), (241) are of course not known explicitly. Fortunately, the calculation of

$$D_{xc}(\mathbf{r}, \mathbf{r}') = -\frac{\delta F_{xc}[\mu[n, \Delta], D[n, \Delta]]}{\delta \Delta^*(\mathbf{r}, \mathbf{r}')} \quad (242)$$

does not require the explicit knowledge of the inverse functionals (240), (241). Knowledge of the direct functionals (238) and (239) is sufficient to calculate D_{xc} by means of implicit functional derivatives. After a tedious calculation, adopting the zero-order functionals (214) and (215) for $n[\mu, D]$ and $\Delta[\mu, D]$ ¹, one finally obtains

$$D_{xc}^{(1)}[\mu, D_s](\mathbf{k}) = n^{(0)} Z_1(\mathbf{k}) \left(V(\mathbf{k}, \mathbf{k}) - \frac{\int d^3 \mathbf{k}_1 V(\mathbf{k}_1, \mathbf{k}_1) Z_0(\mathbf{k}_1)}{\int d^3 \mathbf{k}_2 Z_0(\mathbf{k}_2)} \right) \quad (243)$$

$$D_{xc}^{(2)}[\mu, D_s](\mathbf{k}) = \left(n^{(0)} \right)^2 \left[V(\mathbf{k}, \mathbf{k})^2 Z_2(\mathbf{k}) - Z_1(\mathbf{k}) \frac{\int d^3 \mathbf{k}_2 V(\mathbf{k}_2, \mathbf{k}_2)^2 Z_3(\mathbf{k}_2)}{\int d^3 \mathbf{k}_1 Z_0(\mathbf{k}_1)} \right] \quad (244)$$

with the functions

$$Z_0(\mathbf{k}) = \frac{\beta R_{\mathbf{k}} \tanh(\frac{\beta}{2} R_{\mathbf{k}})}{2 \frac{(\varepsilon_{\mathbf{k}} - \mu)^2}{R_{\mathbf{k}}} \tanh(\frac{\beta}{2} R_{\mathbf{k}}) \cosh^2(\frac{\beta}{2} R_{\mathbf{k}}) + \beta |D_s(\mathbf{k})|^2} \quad (245)$$

$$Z_1(\mathbf{k}) = \frac{(\varepsilon_{\mathbf{k}} - \mu) D_s(\mathbf{k}) \left(\frac{1}{R_{\mathbf{k}}} \tanh(\frac{\beta}{2} R_{\mathbf{k}}) - \frac{\frac{\beta}{2}}{\cosh^2(\frac{\beta}{2} R_{\mathbf{k}})} \right)}{\left(\frac{(\varepsilon_{\mathbf{k}} - \mu)^2}{R_{\mathbf{k}}} \tanh(\frac{\beta}{2} R_{\mathbf{k}}) + \frac{|D_s(\mathbf{k})|^2 \frac{\beta}{2}}{\cosh^2(\frac{\beta}{2} R_{\mathbf{k}})} \right)} \quad (246)$$

$$Z_2(\mathbf{k}) = \frac{D_s(\mathbf{k})}{\frac{(\varepsilon_{\mathbf{k}} - \mu)^2}{R_{\mathbf{k}}} \tanh(\frac{\beta}{2} R_{\mathbf{k}}) + \frac{|D_s(\mathbf{k})|^2 \frac{\beta}{2}}{\cosh^2(\frac{\beta}{2} R_{\mathbf{k}})}} \left[-\frac{(\varepsilon_{\mathbf{k}} - \mu)^2 \beta^2 \tanh(\frac{\beta}{2} R_{\mathbf{k}})}{R_{\mathbf{k}} 8 \cosh^2(\frac{\beta}{2} R_{\mathbf{k}})} + \left(\frac{1}{R_{\mathbf{k}}} \tanh(\frac{\beta}{2} R_{\mathbf{k}}) - \frac{\frac{\beta}{2}}{\cosh^2(\frac{\beta}{2} R_{\mathbf{k}})} \right) \left(\frac{2(\varepsilon_{\mathbf{k}} - \mu)^2 - |D_s(\mathbf{k})|^2}{2R_{\mathbf{k}}^2} \right) \right] \quad (247)$$

¹The influence of higher perturbative contributions to the functionals $n[\mu, D]$ and $\Delta[\mu, D]$ is currently being investigated.

$$\begin{aligned}
Z_3(\mathbf{k}) = & \frac{(\varepsilon_{\mathbf{k}} - \mu)}{\frac{(\varepsilon_{\mathbf{k}} - \mu)^2}{2R_{\mathbf{k}}} \tanh\left(\frac{\beta}{2}R_{\mathbf{k}}\right) + \frac{|D_s(\mathbf{k})|^2 \frac{\beta}{4}}{\cosh^2\left(\frac{\beta}{2}R_{\mathbf{k}}\right)}} \\
& \left[\frac{|D_s(\mathbf{k})|^2}{4R_{\mathbf{k}}^4} \tanh^2\left(\frac{\beta}{2}R_{\mathbf{k}}\right) + \frac{|D_s(\mathbf{k})|^2 \beta \tanh\left(\frac{\beta}{2}R_{\mathbf{k}}\right)}{4R_{\mathbf{k}}^3 \cdot 2 \cosh^2\left(\frac{\beta}{2}R_{\mathbf{k}}\right)} + \right. \\
& \left. + \frac{\frac{\beta^2}{8}}{\cosh^2\left(\frac{\beta}{2}R_{\mathbf{k}}\right)} \left(\tanh^2\left(\frac{\beta}{2}R_{\mathbf{k}}\right) - \frac{|D_s(\mathbf{k})|^2}{R_{\mathbf{k}}^2} \right) \right] \quad (248)
\end{aligned}$$

and

$$R_{\mathbf{k}} = \sqrt{(\varepsilon_{\mathbf{k}} - \mu)^2 + |D_s(\mathbf{k})|^2} . \quad (249)$$

If no external pair field is present, the following gap equation results from (201):

$$D_s(\mathbf{k}) = \frac{1}{2} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} \frac{V(\mathbf{k}, \mathbf{k}') D_s(\mathbf{k}')}{R_{\mathbf{k}'}} \tanh\left(\frac{\beta}{2}R_{\mathbf{k}'}\right) + D_{xc}^{(1)}[D_s] + D_{xc}^{(2)}[D_s] . \quad (250)$$

A numerical solution of this equation is currently under study. We hope that the new exchange-correlation terms will provide a better understanding of the recently discovered high- T_c superconductors.

References

- [1] P. Hohenberg, W. Kohn, Phys. Rev. **136**, B864 (1964)
- [2] W. Kohn, L.J. Sham, Phys. Rev. **140**, A1133 (1965)
- [3] R.O. Jones, O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989)
- [4] B.G. Johnson, P.M.W. Gill, J.A. Pople, J. Chem. Phys. **97**, 7846 (1992)
- [5] E.K.U. Gross, W. Kohn, Adv. Quant. Chem. **21**, 255 (1990)
- [6] G.D. Mahan, K.R. Subbaswamy, *Local Density Theory of Polarizability* (Plenum, New York, 1990)
- [7] R.M. Dreizler, E.K.U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer-Verlag, Berlin, 1990)
- [8] W. Kohn, in *Highlights of Condensed Matter Theory*, ed. by F. Bassani, F. Fumi, M.P. Tosi (North-Holland, Amsterdam, 1985) p.1
- [9] J.E. Harriman, Phys. Rev. **A24**, 680 (1981)
- [10] G. Zumbach, K. Maschke, Phys. Rev. **A28**, 544 (1983); Erratum: Phys. Rev. **A29**, 1585 (1984)
- [11] M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979)
- [12] E.H. Lieb, in *Physics as Natural Philosophy*, ed. by A. Shimony, H. Feshbach (MIT Press, Cambridge) p.111; a revised version appeared in Int. J. Quant. Chem. **24**, 243 (1983) and an extended version in *Density Functional Methods in Physics*, NATO ASI Series B123, ed. by R.M. Dreizler, J. da Providencia (Plenum, New York, 1985) p.31

- [13] P.W. Payne, J. Chem. Phys. **71**, 490 (1979)
- [14] J.D. Talman, W.F. Shadwick, Phys. Rev. **A14**, 36 (1976)
- [15] E. Engel, S.H. Vosko, Phys. Rev. A, in press (1993)
- [16] J.B. Krieger, Y. Li, G.J. Iafrate, Phys. Lett. **A146**, 256 (1990)
- [17] J.B. Krieger, Y. Li, G.J. Iafrate, Phys. Rev. **A45**, 101 (1992)
- [18] U. von Barth, L. Hedin, J. Phys. **C5**, 1629 (1972)
- [19] A.K. Rajagopal, J. Callaway, Phys. Rev. **B7**, 1912 (1973)
- [20] L.M. Sander, H.B. Shore, L.J. Sham, Phys. Rev. Lett. **31**,533 (1973)
- [21] R.K. Kalia, P. Vashishta, Phys. Rev. **B17**, 2655 (1978)
- [22] N.D. Mermin, Phys. Rev. **137**, A1441 (1965)
- [23] M.V. Ramana, A.K. Rajagopal, Adv. Chem. Phys. **54**, 231 (1983)
- [24] A.K. Rajagopal, J. Phys. **C11**, L943 (1978)
- [25] A.H. MacDonald, S.H. Vosko, J. Phys. **C12**, 2977 (1979)
- [26] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. **58**, 1200 (1980)
- [27] J.P. Perdew, A. Zunger, Phys. Rev. **B23**, 5048 (1981)
- [28] J.P. Perdew, R.G. Parr, M. Levy, J.L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982)
- [29] L.J. Sham, M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983)
- [30] J.P. Perdew, M. Levy, Phys. Rev. Lett. **51**, 1884 (1983)
- [31] J.P. Perdew, in *Density Functional Methods in Physics*, NATO ASI Series B123, ed. by R.M. Dreizler, J. da Providencia (Plenum, New York, 1985) p.265
- [32] L.J. Sham, Phys. Rev. **B32**, 3876 (1985)
- [33] L.J. Sham, M. Schlüter, Phys. Rev. **B32**, 3883 (1985)
- [34] W. Hanke, N. Meskini, H. Weiler, in *Electronic Structure, Dynamics, and Quantum Structural Properties of Condensed Matter*, ed. by J.T. Devreese, P. Van Camp, NATO ASI Series B121 (Plenum, New York, 1985) p.113
- [35] W. Kohn, Phys. Rev. **B33**, 4331 (1986)
- [36] J.P. Perdew, Int. J. Quant. Chem. Symp. **19**, 497 (1986)
- [37] L.J. Sham, in *Computational Methods in Band Theory*, ed. by P.J. Marcus, J.F. Janak, A.R. Williams (Plenum, New York, 1971) p.458
- [38] L. Kleinman, Phys. Rev. **B30**, 2223 (1984)
- [39] P.R. Antoniewicz, L. Kleinman, Phys. Rev. **B31**, 6779 (1985)

- [40] L. Kleinman, S. Lee, Phys. Rev. **B37**,4634 (1988)
- [41] J.A. Chevary, S.H. Vosko, Bull. Am. Phys. Soc. **33**, 238 (1988)
- [42] E. Engel, S.H. Vosko, Phys. Rev. **B42**, 4940 (1990)
- [43] S.K. Ma, K.A. Brueckner, Phys. Rev. **165**, 18 (1968)
- [44] M. Rasolt, D.J.W. Geldart, Phys. Rev. Lett. **35**, 1234 (1975)
- [45] M. Rasolt, D.J.W. Geldart, Phys. Rev. **B34**, 1325 (1986)
- [46] D.J.W. Geldart, M. Rasolt, Phys. Rev. **B13**, 1477 (1976)
- [47] D.J.W. Geldart, M. Rasolt, in *The Single-Particle Density in Physics and Chemistry*, ed. by N.H. March, B.M. Deb (Academic, London, 1987) p.151
- [48] D.C. Langreth, J.P. Perdew, Sol. State Comm. **17**, 1425 (1975)
- [49] D.C. Langreth, J.P. Perdew, Phys. Rev. **B15**, 2884 (1977)
- [50] D.C. Langreth, J.P. Perdew, Sol. State Comm. **31**, 567 (1979)
- [51] D.C. Langreth, J.P. Perdew, Phys. Rev. **B21**, 5649 (1980)
- [52] D.C. Langreth, J.P. Perdew, Phys. Rev. **B26**, 2810 (1982)
- [53] D.C. Langreth, M.J. Mehl, Phys. Rev. Lett. **47**, 446 (1981)
- [54] D.C. Langreth, M.J. Mehl, Phys. Rev. **B28**, 1809 (1983); Erratum: Phys. Rev. **B29**, 2310 (1984)
- [55] C.D. Hu, D.C. Langreth, Phys. Script. **32**, 391 (1985)
- [56] C.D. Hu, D.C. Langreth, Phys. Rev. **B33**, 943 (1986)
- [57] A.D. Becke, J. Chem. Phys. **84**, 4524 (1986)
- [58] J.P. Perdew, Y. Wang, Phys. Rev. **B33**, 8800 (1986)
- [59] A.E. DePristo, J.D. Kress, J. Chem. Phys. **86** 1425 (1987)
- [60] S.H. Vosko, L.D. Macdonald, in *Condensed Matter Theories, vol.2*, ed. by P. Vashishta, R.K. Kalia, R.F. Bishop (Plenum, New York, 1987) p.101
- [61] A.D. Becke, Phys. Rev. **A38**, 3098 (1988)
- [62] E. Engel, J.A. Chevary, L.D. Macdonald, S.H. Vosko, Z. Phys. **D23**, 7 (1992)
- [63] C. Lee, W. Yang, R.G. Parr, Phys. Rev. **B37**, 785 (1988)
- [64] J.P. Perdew, Chem. Phys. Lett. **64**, 127 (1979)
- [65] M. Gell-Mann, K.A. Brueckner, Phys. Rev. **106**, 364 (1957)
- [66] E.P. Wigner, Phys. Rev. **46**, 1002 (1934)
- [67] E.P. Wigner, Trans. Farad. Soc. **34**, 678 (1938)

- [68] D.M. Ceperley, B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980)
- [69] R.F. Bishop, K.H. Lüthmann, Phys. Rev. **B17**, 3757 (1978)
- [70] R.F. Bishop, K.H. Lüthmann, Phys. Rev. **B26**, 5523 (1982)
- [71] O. Gunnarsson, B. Lundqvist, Phys. Rev. **B13**, 4274 (1976)
- [72] U. von Barth, Phys. Rev. **A20**, 1693 (1979)
- [73] H. Englisch, R. Englisch, Physica **121A**, 253 (1983)
- [74] J.C. Slater, *The Self-Consistent Field for Molecules and Solids: Quantum Theory of Molecules and Solids, Vol. IV* (McGraw-Hill, New York, 1974)
- [75] J.F. Janak, Phys. Rev. **B18**, 7165 (1978)
- [76] E.K.U. Gross, L.N. Oliveira, W. Kohn, Phys. Rev. **A37**, 2805 (1988)
- [77] A.K. Theophilou, J. Phys. **C12**, 5419 (1979)
- [78] E.K.U. Gross, L.N. Oliveira, W. Kohn, Phys. Rev. **A37**, 2809 (1988)
- [79] W. Kohn, Phys. Rev. **A34**, 737 (1986)
- [80] L.N. Oliveira, E.K.U. Gross, W. Kohn, Phys. Rev. **A37**, 2821 (1988)
- [81] V. Peuckert, J. Phys. **C11**, 4945 (1978)
- [82] A. Zangwill, P. Soven, Phys. Rev. **A21**, 1561 (1980)
- [83] B.M. Deb, S.K. Ghosh, J. Chem. Phys. **77**, 342 (1982)
- [84] S.K. Ghosh, B.M. Deb, Chem. Phys. **71**, 295 (1982)
- [85] S.K. Ghosh, B.M. Deb, Theor. Chim. Acta **62**, 209 (1983)
- [86] S.K. Ghosh, B.M. Deb, J. Mol. Struct. **103**, 163 (1983)
- [87] L.J. Bartolotti, Phys. Rev. **A24**, 1661 (1981)
- [88] L.J. Bartolotti, Phys. Rev. **A26**, 2243 (1982)
- [89] L.J. Bartolotti, J. Chem. Phys. **80**, 5687 (1984)
- [90] L.J. Bartolotti, Phys. Rev. **A36**, 4492 (1987)
- [91] E. Runge, E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)
- [92] A. Toepfer, B. Jacob, H.-J. Lüdde, R.M. Dreizler, Phys. Lett. **93A**, 18 (1982)
- [93] A. Toepfer, H.-J. Lüdde, B. Jacob, R.M. Dreizler, J. Phys. **B18**, 1969 (1985)
- [94] A. Toepfer, A. Henne, H.-J. Lüdde, M. Horbatsch, R.M. Dreizler, Phys. Lett. **A126**, 11 (1987)
- [95] S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982)

- [96] N. Iwamoto, E.K.U. Gross, Phys. Rev. **B35**, 3003 (1987)
- [97] D.M. Ceperley, Phys. Rev. **B18**, 3126 (1978)
- [98] R.W. Shaw, J. Phys. **C3**, 1140 (1970)
- [99] G. Niklasson, Phys. Rev. **B10**, 3052 (1974)
- [100] A.A. Kugler, J. Stat. Phys. **12**, 35 (1975)
- [101] A. Holas, K.S. Singwi, Phys. Rev. **B40**, 158 (1989)
- [102] A.J. Glick, W.F. Long, Phys. Rev. **B4**, 3455 (1971)
- [103] E.K.U. Gross, W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985); Erratum: *ibid.* **57**, 923 (1986)
- [104] N. Iwamoto, Phys. Rev. **A30**, 2597 (1984)
- [105] N. Iwamoto, Phys. Rev. **A30**, 3289 (1984)
- [106] P.F. Byrd, M.D. Friedman, *Handbook of Elliptic Integrals for Engineers and Physicists* (Springer-Verlag, Berlin, 1954)
- [107] B. Dabrowski, Phys. Rev. **B34**, 4989 (1986)
- [108] A. Zangwill, P. Soven, Phys. Rev. Lett. **45**, 204 (1980)
- [109] A. Zangwill, P. Soven, Phys. Rev. **B24**, 4121 (1981)
- [110] Z.H. Levine, P. Soven, Phys. Rev. Lett. **50**, 2074 (1983)
- [111] Z.H. Levine, P. Soven, Phys. Rev. **A29**, 625 (1984)
- [112] A. Liebsch, Phys. Rev. **B36**, 7378 (1987)
- [113] J.F. Dobson, G.H. Harris, J. Phys. **C20**, 6127 (1987)
- [114] J.F. Dobson, G.H. Harris, J.Phys. **C21**, L729 (1988)
- [115] P. Gies, R.R. Gerhardts, Phys. Rev. **B36**, 4422 (1987)
- [116] P. Gies, R.R. Gerhardts, J. Vac. Sci. Technol. **A5**, 936 (1987)
- [117] P. Gies, R.R. Gerhardts, Phys. Rev. **B37**, 10020 (1988)
- [118] K. Kempa, W.L. Schaich, Phys. Rev. **B37**, 6711 (1988)
- [119] T. Ando, Z. Phys. **B26**, 263 (1977)
- [120] Z.H. Levine, D.C. Allan, Phys. Rev. Lett. **63**, 1719 (1989)
- [121] R. Haensel, G. Keitel, P. Schreiber, C. Kunz, Phys. Rev. **188**, 1375 (1969)
- [122] J. Bardeen, L.N. Cooper and J.R. Schrieffer, Phys. Rev. **108**, 1175 (1957)
- [123] H. Fröhlich, Phys. Rev. **79**, 845 (1950)

- [124] L.N. Cooper, Phys. Rev. **104**, 1189 (1956)
- [125] L.N. Oliveira, E.K.U. Gross and W. Kohn, Phys. Rev. Lett. **60**, 2430 (1988)
- [126] L.P. Gorkov, Zh. Eksp. Teor. Fiz. **36**, 1918 (1959) [Sov. Phys. JETP **9**, 1364 (1959)]
- [127] V.L. Ginzburg, L.D. Landau, Zh. Eksp. Teor. Fiz. **20**, 1064 (1950)
- [128] P.G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966)
- [129] W. Kohn, E.K.U. Gross, L.N. Oliveira, J. de Physique (Paris) **50**, 2601 (1989)
- [130] E.K.U. Gross, S. Kurth, Int. J. Quant. Chem. Symp. **25**, 289 (1991)
- [131] N.N. Bogoliubov, Sov.Phys. JETP **7**, 41 (1958)