ON THE QUANTUM FIELD THEORY OF THE INHOMOGENEOUS ELECTRON GAS

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A B S T R A C T

The equilibrium properties of an inhomogeneous gas of interacting fermions are derived using methods of finite temperature quantum field theory. A Landau quasiparticle spectrum yielding the exact ground state energy or, at finite temperatures, the exact thermodynamic potential is constructed from the g -Hartree equations. The heat kernel expansion of Schrödinger operators is then used to express the Hohenberg-Kohn density functional as a series in the quasiparticle density which is asymptotic in the Thomas-Fermi limit. This series is systematically derived from the microscopic action and incorporates boundary effects in an unambiguous manner. The methods developed apply to a large class of field-theoretical models encompassing theories with Yukawa interactions.

1. Introduction

The idea of describing a weakly excited state of a macroscopic body as a quantum mechanical independent particle problem was introduced by Landau¹⁾ in his theory of Fermi liquids. The independent particles, the quasiparticles, move in the volume Ω of the body and are assumed to possess definite energies ϵ and momenta $\mathbf{p}$ with a dispersion $\epsilon(\mathbf{p})$ characteristic for the body under consideration. The fundamental point to realise is that the concept of quasiparticles results within the framework of a quantum theoretical description of collective motion.

In this paper we shall consider systems described by fermion quasiparticle excitations and shall point out a procedure to construct a quasiparticle basis from the Hamiltonian of the system. Although the methods we are going to develop are more general, we shall confine our attention to a system of electrons interacting by Coulomb interaction and electrically neutralised by fixed positively charged external sources: the inhomogeneous electron gas.

Mean field expansions in the context of a functional integral formulation of quantum field theory (QFT) have gained great importance. They led to quasi-classical approximations in QFT²⁾ and were shown³⁾ to play an instrumental role in the description of nuclear phenomena. We have employed⁴⁾ these concepts to a mean field description of atoms and, in particular, have shown that the mean field, determined as the stationary point of the probability measure in field space, is non-unique. The non-uniqueness is a consequence of the lack of normal-ordering in functional integrals and is parametrised by a parameter g : the mean field is calculated from the g -Hartree equation. Optimising the mean field by choosing $g=g_0$ such that the g -Hartree energy is the exact total energy of the system, has been shown⁵⁾⁶⁾ to be a successful concept for the description of atomic states. The method can be extended to relativistic systems⁷⁾. In terms of Feynman graphs, non-normal ordering expresses itself in the appearance of tadpole graphs, the partial

summation of the latter establishes⁵⁾ a connection between the g-Hartree and traditional Hartree-Fock methods.

Here, our main concern is the discussion of the equilibrium properties of the inhomogeneous electron gas within the scope of the g-Hartree approach. First we show that in the equilibrium state, imposed by antiperiodic temporal boundary conditions (we only consider fermions), mean-fields are time-independent (the importance of time-dependent mean-fields pertaining to non-equilibrium states has been emphasised in ref.(8)). Two choices of g are now possible

$$(i) \quad g = g_0 : \quad \{\epsilon_\alpha\} \quad (1.1)$$

$$(ii) \quad g = g_1 : \quad \{\epsilon_\alpha^{(1)}\}$$

(yielding spectra $\{\epsilon_\alpha\}$ and $\{\epsilon_\alpha^{(1)}\}$ defined by the g-Hartree equation) such that the exact grand canonical potential is given as

$$(i) \quad K = -\beta^{-1} \sum_\alpha \ln (1 + e^{-\beta \epsilon_\alpha}) + K_{g-H} \quad (1.2)$$

$$(ii) \quad K = -\beta^{-1} \sum_\alpha \ln (1 + e^{-\beta \epsilon_\alpha^{(1)}})$$

where β^{-1} is the temperature and K_{g-H} the explicitly known contribution of the g-Hartree mean field. It is the close resemblance of K to the grand canonical potential of the free Fermi gas which leads us to identify $\{\epsilon_\alpha\}$ or $\{\epsilon_\alpha^{(1)}\}$ with the Landau quasiparticle spectrum.

To get a more detailed insight into the machinery of the method we then use the representation (1.2) to construct K in terms of the quasiparticle density $n(\vec{x})$ as a series which is asymptotic in

the Thomas-Fermi limit⁹⁾. For $\beta^{-1} = 0$, i.e. for the ground state, an asymptotic expansion of the Hohenberg-Kohn energy-density functional obtains. The important point to be stressed here is that this series appears as a systematic expansion of the exact energy with coefficients determined by the Lagrangian of the system, i.e. by its microscopically formulated interactions. The quasiparticle density $n(\vec{x})$ and the equilibrium density

$$n_{\text{obs}}(\vec{x}) = \frac{\delta k}{\delta \mu(\vec{x})},$$

where $\mu(\vec{x})$ is the space-dependent chemical potential, are related by the theory in a well-defined manner.

The material of the paper is organised in four sections. In chapter 2 we derive the g-Hartree representations (1.2). General thermodynamic considerations and the Thomas-Fermi type series for the grand canonical potential or, at $\beta^{-1} = 0$, the energy are derived in chapter 3 with the help of the heat kernel expansion for Schrödinger operators. In chapter 4, we collect our conclusions. In the attempt to achieve a rather self-contained presentation, we added an Appendix in which the calculation of regularised and renormalised fermionic determinants in terms of Floquet indices is described.

2. The g-Hartree basis at finite temperature

The equilibrium properties of an inhomogeneous electron gas enclosed in a volume Ω at temperature β^{-1} are characterised by a space-dependent chemical potential $\mu(\vec{x})$ which acts as an external potential. The description starts from the partition function of the system which, for a grand canonical ensemble, is a function of β and Ω and a functional of $\mu(\vec{x})$

$$\begin{aligned}
 Z &= \text{tr} \left(e^{-\beta \left(H - \int_{\Omega} \mu(\vec{x}) n_{\text{obs}}(\vec{x}) \right)} \right) \\
 (2.1) \quad &= Z[\mu(\vec{x}); \beta, \Omega]
 \end{aligned}$$

where H is the Hamiltonian of the system and $n_{\text{obs}}(\vec{x})$ the particle density.

In this chapter we are going to show that the partition function for a system of interacting electrons can be exactly calculated as the partition function of a free quasi-particle gas. We give equations determining this independent quasi-particle basis, the g-Hartree basis at finite temperatures. Stated differently, we explicitly verify Landau's original picture¹⁾ of quasiparticle excitations in quantum Fermi liquids in a way which, seen from a practical standpoint, is accessible to actual numerical calculations.

The starting point of our discussion is the usual functional integral representation of Z

$$(2.2) \quad Z = \int_{\text{antiperiodic}} \mathcal{D}\psi \int \mathcal{D}\psi^* e^{S[\psi, \psi^*]},$$

$\psi(\vec{x}, t)$ is a fermionic field and has to be treated as a Grassmannian variable to account for the Pauli exclusion principle, integration over antiperiodic configurations guarantees the correct KMS boundary conditions. The (euclidean) action S describes the Coulomb interaction of electrons and the interaction with the chemical potential $\mu(\vec{x})$

$$\begin{aligned}
 S &= \int_0^\beta d\tau \int_{\Omega} d^3x \, \psi^*(\vec{x}, \tau) \cdot (-\partial_\tau - D) \psi(\vec{x}, \tau) \\
 (2.3) \quad &- \frac{1}{2} \int_0^\beta d\tau \int_{\Omega} d^3x \int_{\Omega} d^3x' \, |\psi(\vec{x}, \tau)|^2 V(\vec{x}, \vec{x}') |\psi(\vec{x}', \tau)|^2
 \end{aligned}$$

with

$$V(\vec{x}, \vec{x}') = \frac{e^2}{4\pi \cdot |\vec{x} - \vec{x}'|}$$

and

$$D = D_{kin} + \mu(\vec{x}),$$

the operator D_{kin} is the non-relativistic (or relativistic) kinetic energy of the electron.

Employing the Hubbard-Stratonovitch identity to derive a generalised Siegert¹¹⁾ representation we obtain⁴⁾

$$Z = \int_{\text{periodic}} D\varphi e^{-\frac{1}{2} \int_0^\beta d\tau \int d^3x \varphi(\vec{x}, \tau) V^{-1} \varphi(\vec{x}, \tau) \cdot \det(-\partial_\tau - D - \varphi)},$$

where V^{-1} is the operator inverse of the electron-electron interaction $e^2 V^{-1} = -\Delta$, and, employing (A.30),

$$(2.4) \quad Z = \int_{\text{periodic}} D\varphi e^{-\frac{1}{2} \int \varphi V^{-1} \varphi - \sum_{\alpha} \ln(1 + e^{-\beta \varepsilon_{\alpha}(\beta)})}$$

The pseudo-energy levels $\varepsilon_{\alpha}(\beta)$ are functionals of $\varphi(\vec{x}, \tau)$ and are to be determined from the Floquet indices $\tilde{\varepsilon}_{\alpha}(\tau)$

$$(2.5) \quad (i\partial_t - D - \tilde{\varphi}(\vec{x}, t)) \tilde{u}_{\alpha}(\vec{x}, t) = -\tilde{\varepsilon}_{\alpha}(\tau) \tilde{u}_{\alpha}(\vec{x}, t)$$

with

$$\tilde{\mu}_{\alpha}(\vec{x}, t) = \tilde{\mu}_{\alpha}(\vec{x}, t + T)$$

and

$$(2.6) \quad \int_0^{\beta} d\tau \int_{\Omega} d^3x \quad |\mu_{\alpha}(\vec{x}, \tau)|^2 = 1$$

by the analytic continuation (A.24)

$$(2.7) \quad \mathcal{E}_{\alpha}(\beta) = \tilde{\mathcal{E}}_{\alpha}(-i\beta).$$

An important point has to be mentioned in this context: the integration variable $\mathcal{Y}(\vec{x}, \tau)$ in equation (2.4) is real by construction⁴⁾, the continuation

$$(2.8) \quad \tilde{\mathcal{Y}}(\vec{x}, t) := \mathcal{Y}(\vec{x}, -it)$$

used in the determination of the Floquet indices, however, will be complex in general such that the "eigenvalue" problem (2.5) requires particular attention and generally yields complex indices $\tilde{\mathcal{E}}_{\alpha}(\tau)$. We shall soon encounter this problem.

The representation (2.4) has a transparent interpretation as a Gaussian average, with weight V^{-1} , of the partition function of a gas of free electrons in a dissipative, periodic external field $\mathcal{Y}(\vec{x}, \tau)$. We now follow the usual line of argumentation and determine the stationary configuration $\mathcal{Y}^{(0)}$ in (2.4) which is assumed to saturate this functional integral such that deviations from it can be treated

perturbatively.

From (2.4) we get immediately

$$(2.9) \quad (V^{-1} \varphi^{(0)}) (\vec{x}, \tau) = \sum \frac{\beta}{e^{\beta \epsilon_\alpha + 1}} |\mu_\alpha(\vec{x}, \tau)|^2$$

(from (2.5) we have $\frac{\delta}{\delta \varphi(\vec{x}, t)} \tilde{\epsilon}_\alpha(\tau) = |\tilde{\mu}_\alpha(\vec{x}, t)|^2$ and by continuation of (2.5) $\frac{\delta \epsilon_\alpha(\beta)}{\delta \varphi(\vec{x}, t)} = |\mu_\alpha(\vec{x}, \tau)|^2$ with $\tilde{\mu}_\alpha(\vec{x}, -i\tau) = \mu_\alpha(\vec{x}, \tau)$) or

$$(2.10) \quad \varphi^{(0)}(\vec{x}, \tau) = \beta \sum_\alpha n_\alpha \int_{\Omega} d^3x' V(\vec{x}, \vec{x}') |u_\alpha(\vec{x}', \tau)|^2$$

where n_α is the Fermi distribution at temperature β^{-1} . Clearly, $\varphi^{(0)}(\vec{x}, \tau)$ is a τ -dependent Hartree field. Writing the interaction term in the action (2.3) as a sum of direct and exchange interactions (see equations (2.27)-(2.32) of ref. 4a), (2.10) generalises to the g-Hartree potential

$$(2.11) \quad \varphi^{(0)}(\vec{x}, \tau) = \beta \sum_\alpha n_\alpha \int_{\Omega} d^3x' V(\vec{x}, \vec{x}') \cdot \left\{ g |\mu_\alpha(\vec{x}', \tau)|^2 - (1-g) \mu_\alpha^*(\vec{x}', \tau) \mu_\alpha(\vec{x}, \tau) * \right\},$$

the star indicates the usual exchange convolution, g is a parameter which can be chosen ad libitum, a freedom which will become essential soon.

It is now important to verify the consistency of the potentials (2.10) and (2.11) which, by construction of (2.4), have to be real or hermitian (as far as the exchange convolution is concerned)

respectively. It is immediately seen that this is the case if the $\varepsilon_\alpha(\beta)$ are real. On the other hand, analytically continuing (2.5) and (2.6) by (2.7) and (2.8) we see that the latter are determined by

$$(2.12) \quad (-\partial_\tau - \mathcal{D} - \varphi(\vec{x}, \tau)) \mu_\alpha(\vec{x}, \tau) = -\varepsilon_\alpha(\beta) \mu_\alpha(\vec{x}, \tau)$$

and

$$\mu_\alpha(\vec{x}, \tau) = \mu_\alpha(\vec{x}, \tau + \beta),$$

i.e. by a non-hermitian operator.

Since, however,

$$\int_0^\beta d\tau \mu_\alpha^*(\vec{x}, \tau) \partial_\tau \mu_\alpha(\vec{x}, \tau) = 0$$

for real, periodic functions μ_α , the spectrum $\varepsilon_\alpha(\beta)$ will be real if reality of the solutions of (2.12) is demanded. Then the τ -dependence of the $\mu_\alpha(\vec{x}, \tau)$ is essentially parametric because the μ_α can be determined by extremalising the functional (defined over the set of real, periodic functions)

$$(2.13) \quad \begin{aligned} \mathcal{F}[\mu_\alpha] &= \iint \mu_\alpha (\partial_\tau + \mathcal{D} + \varphi_0 - \varepsilon_\alpha) \mu_\alpha \\ &= \int d\tau \int d^3x \mu_\alpha(\vec{x}, \tau) \{ \mathcal{D} + \varphi^{(0)}(\vec{x}, \tau) - \varepsilon_\alpha(\beta) \} \mu_\alpha(\vec{x}, \tau) \end{aligned}$$

Now let

$$\mu_{\alpha_0}(\vec{x}) := \mu_\alpha(\vec{x}, \tau_0)$$

be such an extremum; then $\mu_{\alpha_0}(\vec{x})$ obeys

$$(2.14) \quad \{D + \varphi^{(0)}\} \mu_{\alpha_0}(\vec{x}) = \varepsilon_{\alpha}(\beta) \mu_{\alpha_0}(\vec{x})$$

which is the " τ -independent" g-Hartree equation. If $\mu_{\alpha}(\vec{x}, \tau)$ is a continuous parametrisation of a set of solutions of periodic, real $\mu_{\alpha}(\vec{x}, \tau)$ of (2.14) we should find "nearby" solutions $\mu_{\alpha}(\vec{x}, \tau_0 + d\tau)$. We try to construct such a solution in the following manner. We expand in terms of modes to implement periodicity

$$(2.15) \quad \mu_{\alpha}(\vec{x}, \tau) = \frac{1}{\sqrt{\beta}} \sum_{m=-\infty}^{+\infty} \bar{\mu}_{\alpha m}(\vec{x}) e^{-\frac{2\pi i m}{\beta} \cdot \tau}$$

with

$$(2.16) \quad \bar{\mu}_{\alpha m}(\vec{x}) = \bar{\mu}_{\alpha - m}^*(\vec{x})$$

because of reality. We then identify the solution $\mu_{\alpha_0}(\vec{x})$ of (2.13) with the zero mode $\bar{\mu}_{\alpha_0}(\vec{x})$ of this expansion

$$(2.17) \quad \bar{\mu}_{\alpha_0}(\vec{x}) = \mu_{\alpha_0}(\vec{x})$$

insert into (2.12) and take the $\bar{\mu}_{\alpha k}(\vec{x}), |k| \geq 1$ up to linear terms since we are looking for "nearby" solutions, i.e. small $\bar{\mu}_{\alpha k}, |k| \geq 1$. A simple calculation yields

$$(2.18) \quad \left(\mathcal{D} + \mathcal{Y}^{(0)} + \left(\frac{2\pi k}{\beta} \right)^2 (\mathcal{D} + \mathcal{Y}^{(0)} - \bar{\varepsilon}_\alpha)^{-1} - \bar{\varepsilon}_\alpha \right) \bar{\mu}_{\alpha k} = 0$$

$$|k| \geq 1$$

which, with (the $\mu_{\mathcal{P}0}$ obey (2.14))

$$\bar{\mu}_{\alpha k}(\vec{x}) =: \sum_{\mathcal{P}} a_{\alpha k}^{(\mathcal{P})} \mu_{\mathcal{P}0}(\vec{x}),$$

turns into

$$a_{\alpha k}^{(\mathcal{P})} \left\{ (\varepsilon_{\mathcal{P}} - \bar{\varepsilon}_\alpha) + \left(\frac{2\pi k}{\beta} \right)^2 \frac{1}{\varepsilon_{\mathcal{P}} - \bar{\varepsilon}_\alpha} \right\} = 0.$$

Since $\bar{\varepsilon}_\alpha$ is required to be real, the only solution is

$$a_{\alpha k}^{(\mathcal{P})} = 0$$

and no "nearby" solutions exist.

Summarising the content of the last paragraph we reemphasise the essential ingredient, the reality of the spectrum $\varepsilon_\alpha(\beta)$, from which our deductions started. The first conclusion was that the $\mu_\alpha(\vec{x}, \tau)$ had to be real which in turn led to a τ - independent non-linear equation determining the spectrum $\varepsilon_\alpha(\beta)$, the g-Hartree equation. An eventually remaining τ -dependence was at most parametric, i.e. it "enumerates" simply different solutions. Furthermore, we showed that no "nearby" solutions exist.

We write the g-Hartree equation (2.14) in an explicit form

$$(2.19) \quad \left\{ \mathcal{D}_{kin} + \mu(\vec{x}) + \sum_{\alpha} n_{\alpha} \int d^3x' V(\vec{x}, \vec{x}') \cdot \right. \\ \left. \cdot (g |\psi_{\alpha}(\vec{x}')|^2 - (1-g) \psi_{\alpha}^*(\vec{x}') \psi_{\alpha}(\vec{x}') *) \right\} \mu_{\gamma}(\vec{x}) = \varepsilon_{\gamma}(\beta) \mu_{\gamma}(\vec{x})$$

this equation defines an independent fermion quasiparticle basis. The temperature dependence of the spectrum $\varepsilon_{\alpha}(\beta)$, $\mu_{\alpha}(\vec{x})$ arises from the selfconsistent Fermi distribution n_{α} .

The Ω - dependence in (2.14) needs some further consideration. Two cases are physically relevant.

- (i) The chemical potential $\mu(\vec{x})$ is confining, i.e.
 $\mu(\vec{x}) \rightarrow \infty$ for $|\vec{x}| \rightarrow \infty$.
- (ii) $\mu(\vec{x})$ tends to a finite value, i.e. $\mu(\vec{x}) \rightarrow \mu < \infty$ for $|\vec{x}| \rightarrow \infty$.

The first case can be visualised e.g. by a hard-wall potential enclosing a finite volume or an oscillator-like potential $\mu(\vec{x}) \sim |\vec{x}|^2$ for large $|\vec{x}|$. The second case encompasses atoms and molecules. For (i) the limit $\Omega \rightarrow \infty$ is without problems, a discrete spectrum $\varepsilon_{\alpha}(\beta)$ results. In the second case "screening" is employed¹²⁾ and the system is enclosed in a large but finite box, without this precaution continuum states will appear in the tail of the finite temperature Fermi-distribution in (2.19) and render this equation (superficially) ill-defined in the limit $\Omega \rightarrow \infty$.

The usual procedure is now to expand quantum fields in this quasiparticle basis and to formulate a perturbation theory. In the context of our functional formulation this simply means to expand the integrand of (2.4) around $\varphi^{(0)}$ to get

$$(2.20) \quad Z = Z_0 \cdot Z_{corr}$$

where

$$(2.21) \quad \ln Z_0 = - \sum_{\alpha} \ln (1 + e^{-\beta \epsilon_{\alpha}(\beta)}) - \frac{\beta}{2} \{ g \cdot \text{O} \text{---} \text{O} - (1-g) \text{---} \text{O} \}$$

and

$$(2.22) \quad \begin{aligned} \ln Z_{\text{corr}} = & -\beta \left\{ \frac{1-g}{2} \text{O} \text{---} \text{O} - \frac{g}{2} \text{---} \text{O} - \right. \\ & - \frac{g^2}{2} \text{---} \text{O} \text{---} \text{O} + g(1-g) \text{---} \text{O} \text{---} \text{O} - \frac{(1-g)^2}{2} \text{O} \text{---} \text{O} \text{---} \text{O} \\ & \left. - \frac{1}{4} \text{---} \text{O} \text{---} \text{O} + \frac{1}{4} \text{---} \text{O} \text{---} \text{O} + O(V^3) \right\}. \end{aligned}$$

The following Feynman rules are to be used to compute these graphs (integration $\int d^3x \int_0^{\beta} d\tau$ is understood)

$$(2.23) \quad \begin{aligned} \text{---} \text{O} \text{---} \text{O} & : V(\vec{x}, \vec{x}') \delta(\tau - \tau') \\ \text{---} \text{O} & : g_{Y(0)}(\vec{x}, \tau; \vec{x}', \tau') = \sum_{\alpha} u_{\alpha}(\vec{x}) \mu_{\alpha}^*(\vec{x}') e^{-\epsilon_{\alpha}(\beta)(\tau - \tau')} \\ & \cdot \{ \theta(\tau - \tau') - n_{\alpha} \} \end{aligned}$$

the fermion propagator $g_{Y(0)}$ follows from the solution of (2.19). Details are to be found in refs. (4a, 4b).

It is of central importance to realise that in (2.20) Z is g -independent, it is the relative weight of Z_0 and Z_{corr} which is controlled by the choice of g . In particular we have shown⁴⁾⁵⁾ and explored that for the ground state of atoms ($\beta \rightarrow \infty$, $\mu(\vec{x}) = V_{\text{nuc}}(\vec{x}) = -\frac{Ze^2}{r}$) a unique choice $0 \leq g_0 \leq 1$ of g is possible such that

$$(2.24) \quad Z_{\text{corr}} \Big|_{g=g_0} = 1$$

which means that for $g=g_0$ all quantum fluctuations contributing to the partition function, i.e. the (grand canonical) thermodynamic potential, vanish: equilibrium properties are exactly given by an independent quasiparticle basis obtained from (2.19) with $g=g_0$.

It is a very plausible hypothesis to assume these notions to be valid for a larger class of physical systems at finite temperatures characterised by various ansätze for the chemical potentials: multi-centered (molecules), periodic (crystals), with randomly distributed centers (amorphous substances), liquids etc. Its plausibility stems from the fact that g controls the strength of the direct potential and tunes the potential $\ln Z_0$ in a wide range.

Hence, we postulate that under the just mentioned specifications there exists a functional

$$(2.25) \quad g_0 = g_0 [\mu(\vec{x}); \beta, \Omega]$$

such that

$$(2.26) \quad Z_{\text{corr}} \Big|_{g=g_0} = 1.$$

The independent quasiparticle basis originally introduced by Landau is then constructed by solving (2.19) with this g_0 . From this basis the exact grand canonical potential and, therefore, all equilibrium properties

of our inhomogeneous gas of interacting electrons can be constructed.

The problem is, of course, to find the functional (2.25). Two procedures seem viable: g_0 can be determined phenomenologically or (2.26) can be used as an equation to calculate g_0 , e.g. in k -th order perturbation theory. Both ways were shown⁵⁾⁶⁾ to be very effective for atoms.

Before proceeding to the next chapter where we discuss the thermodynamics of the inhomogeneous electron gas in more detail, we should mention the connection, established elsewhere⁵⁾, of the g -Hartree and Hartree-Fock basis. Both are obtained by extremalising different functionals connected by infinite summation of tad-pole contributions. In a purely field-theoretic operator language, the summing of tadpoles restores normal-ordering which is originally not implemented in the functional integral representation of Green's functions. Seen from this angle, it is well understood that the latter yields g -Hartree rather than Hartree-Fock equations (which, after tad-pole summation correspond to $g=0$ and, therefore, to the normal ordering case).

3. Thermodynamics of the inhomogeneous electron gas in the g_0 -Hartree basis

Thermodynamic properties are now straightforwardly derived from the grand canonical potential K which we obtain from (2.21) and (2.26). Explicitly we have

$$\begin{aligned}
 K &= \beta^{-1} \ln Z = \beta^{-1} \ln Z_0 \\
 (3.1) \quad &= -\beta^{-1} \sum_{\alpha} \ln (1 + e^{-\beta \epsilon_{\alpha}}) - \frac{1}{2} \int d^3x \sum_{\gamma} n_{\gamma} \psi_{\gamma}^*(\vec{x}) \mathcal{V}_{g_0}(\vec{x}) \psi_{\gamma}(\vec{x})
 \end{aligned}$$

where

$$(3.2) \quad \mathcal{V}_{g_0}(\vec{x}) = \int d^3x' V(\vec{x}, \vec{x}') \sum_{\alpha} n_{\alpha} \{ g_0 |\psi_{\alpha}(\vec{x}')|^2 - (1-g_0) \psi_{\alpha}(\vec{x}) \psi_{\alpha}^*(\vec{x}') \}$$

is the g -Hartree potential taken at the value (2.25) and $\varepsilon_{\alpha}, \psi_{\alpha}(\vec{x})$ are solutions of the g_0 -Hartree equations and, therefore, functionally dependent on β, Ω and $\mu(\vec{x})$; n_{α} is the Fermi distribution

$$(3.3) \quad n_{\alpha} = \frac{1}{e^{\beta \varepsilon_{\alpha}} + 1}.$$

Now let g be one of the parameters on which $g_0, \varepsilon_{\alpha}, \psi_{\alpha}$ depend. From the g_0 -Hartree equation

$$(3.4) \quad (D_{\text{kin}} + \mu(\vec{x}) + \mathcal{V}_{g_0}(\vec{x})) \psi_{\alpha}(\vec{x}) = \varepsilon_{\alpha} \psi_{\alpha}(\vec{x})$$

we immediately get

$$(3.5) \quad \frac{\partial \varepsilon_{\alpha}}{\partial g} = \int d^3x \psi_{\alpha}^*(\vec{x}) \left(\frac{\partial}{\partial g} \mathcal{V}_{g_0}(\vec{x}) \right) \psi_{\alpha}(\vec{x});$$

Furthermore, taking into account the explicit form (3.2) for $\mathcal{V}_{g_0}(\vec{x})$, we find

$$\begin{aligned}
 & \frac{\partial}{\partial g} \int d^3x \sum_f n_f \psi_f^*(\vec{x}) \psi_f(\vec{x}) \\
 (3.6) \quad & = 2 \int d^3x \sum_f n_f \psi_f^*(\vec{x}) \left(\frac{\partial}{\partial g} \psi_f(\vec{x}) \right) \psi_f(\vec{x}) - \frac{\partial g_0}{\partial g} B
 \end{aligned}$$

with

$$\begin{aligned}
 B &= \int d^3x \int d^3x' V(\vec{x}, \vec{x}') \sum_{\alpha, \gamma} n_{\alpha} n_{\gamma} \cdot \\
 (3.7) \quad & \cdot \left\{ |\psi_{\alpha}(\vec{x})|^2 |\psi_{\gamma}(\vec{x}')|^2 + \psi_{\alpha}(\vec{x}) \psi_{\alpha}^*(\vec{x}') \psi_{\gamma}(\vec{x}') \psi_{\gamma}^*(\vec{x}) \right\}.
 \end{aligned}$$

These formulae can be used to compute the observed local density of our system

$$\begin{aligned}
 (3.8) \quad n_{obs}(\vec{x}) &= \frac{\delta k}{\delta \mu(\vec{x})} = \sum_{\alpha} n_{\alpha} |\psi_{\alpha}(\vec{x})|^2 + \frac{\beta}{2} \frac{\delta g_0}{\delta \mu(\vec{x})} B \\
 &= : n(\vec{x}) + \frac{\beta}{2} \frac{\delta g_0}{\delta \mu(\vec{x})} \cdot B;
 \end{aligned}$$

we discover the intuitively clear fact that in the quasiparticle picture the difference between the observed density $n_{obs}(\vec{x})$ and the quasiparticle density $n(\vec{x})$ is determined by the functional $g_0[\mu(\vec{x}); \beta, \mathcal{Q}]$ which, by construction, parametrises correlations.

The two equations

$$(3.9) \quad N = \int d^3x n_{obs}(\vec{x}) = N[\mu(\vec{x}); \beta, \mathcal{Q}]$$

and

$$(3.10) \quad P \cdot \Omega = -K = -K[\mu(\vec{x}); \beta, \Omega]$$

where P is the pressure of the system and Ω its volume, define functionals $\mu(\vec{x}) \mapsto N$ and $\mu(\vec{x}) \mapsto K$ from which the equation of state can be derived in the usual manner. Define the Fermi energy of the quasiparticle distribution by

$$(3.11) \quad \mu(\vec{x}) = \varepsilon_F + \mu_0(\vec{x})$$

with

$$\mu_0(\vec{x}) \rightarrow 0 \quad ; \quad |\vec{x}| \rightarrow \infty$$

then the equation of state is obtained by eliminating ε_F from (3.9) and (3.10) as a relation

$$(3.12) \quad F[\mu_0(\vec{x}); P, \Omega, \beta, N] = 0.$$

On the other hand, we can make use of the local structure of equ.(3.8) which defines for each $\vec{x}$ a functional $\mu(\vec{y}) \mapsto n_{obs}(\vec{x})$ and which we write as

$$n_{obs} = n_{obs}[\mu(\vec{y}); \vec{x}];$$

inverting this relation to obtain

$$\mu = \mu [n_{\text{obs}}(\vec{y}); \vec{x}]$$

and inserting in (3.10) we finally get a functional

$$(3.13) \quad K = \tilde{K} [n_{\text{obs}}(\vec{y}); \beta, \Omega] = -P\Omega;$$

for $\beta \rightarrow \infty$, i.e. for the ground state, this functional coincides with the energy density functional which received broad attention in the literature⁹⁾.

The construction of $\tilde{K}$ in terms of the parameters of the action (2.3) is indeed a formidable task. Even for the free inhomogeneous electron gas, i.e. the electron-electron interaction $V(\vec{x}, \vec{x}') = 0$, a closed expression is not known.

We shall present an asymptotic construction of $\tilde{K}$ which relies on the heat kernel expansion of Schrödinger operators. It is asymptotic in the Thomas-Fermi limit and allows for the systematic calculation of "correction terms" to the latter. For the sake of clarity we proceed in two steps: as an illustration of the general method we first treat the free case, the g-Hartree case for $g=g_0$ is then considered in a separate section.

Before doing so, it might be useful to point out an alternative definition of an optimised mean field. Instead of defining the functional (2.25) by (2.26) we can define a new functional

$$(3.14) \quad g_1 = g_1 [\mu(\vec{x}); \beta, \Omega]$$

as a solution of

$$(3.15) \quad \left(\ln Z^{\text{corr}} - \frac{\beta}{2} \int d^3x \sum_f n_f \psi_f^*(\vec{x}) \mathcal{U}_g(\vec{x}) \psi_f(\vec{x}) \right) \Big|_{g=g_1} = 0.$$

The grand canonical potential is then given by

$$(3.16) \quad K = -\beta^{-1} \sum_{\alpha} \ln(1 + e^{-\beta \varepsilon_{\alpha}^{(1)}})$$

where the spectrum $\varepsilon_{\alpha}^{(1)}$ is to be determined from g-Hartree equations for $g=g_1$

$$(3.17) \quad (\mathcal{D}_{\text{kin}} + \mu(\vec{x}) + \mathcal{U}_{g_1}(\vec{x})) \psi_{\alpha}^{(1)}(\vec{x}) = \varepsilon_{\alpha}^{(1)} \psi_{\alpha}^{(1)}(\vec{x}).$$

The advantage of this definition obviously is its similarity to the free case.

Of course, the observed density $n_{\text{obs}}^{(1)}$ and the quasiparticle density

$$(3.18) \quad n^{(1)}(\vec{x}) = \sum_f n_f |\psi_f^{(1)}(\vec{x})|^2$$

still differ. Using (3.5) we immediately find

$$(3.19) \quad n_{\text{obs}}^{(1)}(\vec{x}) = \frac{\delta K}{\delta \mu(\vec{x})} = n^{(1)}(\vec{x}) + \beta \sum_{\alpha} n_{\alpha} \int d^3x' \psi_{\alpha}^{(1)*}(\vec{x}') \frac{\delta \mathcal{U}_{g_1}(\vec{x}')}{\delta \mu(\vec{x})} \psi_{\alpha}^{(1)}(\vec{x}').$$

After this digression we return to our main line of argument and begin with

- a) Thomas-Fermi type asymptotic expansions for the free inhomogeneous electron gas.

Translating summations into integrations we have

$$(3.20) \quad K = -\beta^{-1} \frac{\Omega}{(2\pi)^3} \int dE \, g(E) \ln(1 + e^{-\beta(E - \epsilon_F)})$$

and

$$(3.21) \quad n(\vec{x}) = \frac{\Omega}{(2\pi)^3} \int dE \, \frac{g(E)}{e^{\beta(E - \epsilon_F)} + 1} |\psi_E(\vec{x})|^2$$

where the Fermi energy ϵ_F is defined as in (3.11). The problem is, of course, to determine the spectral density $g(E)$ from the Schrödinger equation (units $2m = \hbar = 1$)

$$(3.22) \quad (-\Delta + \mu_0(\vec{x})) \psi_E(\vec{x}) = E \psi_E(\vec{x}).$$

We start from its definition

$$(3.23) \quad g(E) |\psi_E(\vec{x})|^2 = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} dt \, \langle x | e^{-(\Delta + \mu_0)t} | x \rangle e^{Et}$$

and observe that the small- t behaviour of $\langle x | e^{-Ht} | x \rangle$ ($H = -\Delta + \mu_0(\vec{x})$) yields an asymptotic expansion of $g(E) |\psi_E(\vec{x})|^2$ for large E . The former is given by the Seeley expansion of the

heat kernel¹³⁾ $\langle x | e^{-Ht} | y \rangle$ which obeys

$$\left(\frac{\partial}{\partial t} + H \right) \langle x | e^{-Ht} | y \rangle = 0$$

with

$$\langle x | e^{-Ht} | y \rangle \xrightarrow[t \rightarrow +0]{} \delta(\vec{x} - \vec{y})$$

For $t \rightarrow +0$, the following asymptotic expansion holds

$$\langle x | e^{-tH} | y \rangle \underset{t \rightarrow +0}{\sim} \left(\frac{1}{4\pi t} \right)^{3/2} e^{-\frac{(\vec{x}-\vec{y})^2}{4t}}.$$

$$(3.24) \quad \cdot \left\{ \sum_{k=0}^{\infty} t^k a_k(\vec{x}, \vec{y}) + \sum_{k=0}^{\infty} t^{k+\frac{1}{2}} b_k(\vec{x}, \vec{y}) \right\};$$

the kernel is taken to be defined on a compact manifold with boundary, the latter induces the coefficients b_k . We take a sphere with radius R and assume Dirichlet boundary conditions and compute¹⁴⁾ at first the diagonal elements required for the determination of $S(E)$

$$(3.25) \quad \begin{aligned} a_1(\vec{x}, \vec{x}) &= -\mu_0(\vec{x}) \\ a_2(\vec{x}, \vec{x}) &= \frac{1}{2} \mu_0^2(\vec{x}) - \frac{1}{6} \Delta \mu_0(\vec{x}) \\ b_1(\vec{x}, \vec{x}) &= - (4\pi)^{3/2} R^2/4 \delta(|\vec{x}| - R) \\ b_2(\vec{x}, \vec{x}) &= (4\pi)^{3/2} \left(-\frac{1}{48} + \frac{1}{16\pi} \mu_0(\vec{x}) \right) (|\vec{x}|^2 \sin \theta) \delta(|\vec{x}| - R), \end{aligned}$$

θ is, of course, the polar angle of $\vec{x}$.

Using (the factor $(2\pi)^3 \Omega^{-1}$ appears because of continuum normalisation of $|x\rangle$)

$$(3.26) \quad \mathcal{G}(E) = \frac{(2\pi)^3 \Omega^{-1}}{2\pi i} \int_{C-i\infty}^{C+i\infty} d^3x \int dt e^{Et} \langle x | e^{-Ht} | x \rangle$$

we have for large E

$$(3.27) \quad \begin{aligned} \frac{\Omega \mathcal{G}(E)}{(2\pi)^3} &\sim \frac{2}{(4\pi)^{3/2}} \left\{ \frac{E^{1/2}}{\Gamma(3/2)} + \frac{E^0}{\Gamma(1)} \int d^3x b_1(\vec{x}, \vec{x}) \right. \\ &+ \frac{E^{-1/2}}{\Gamma(1/2)} \int d^3x a_1(\vec{x}, \vec{x}) + \mathcal{G}(E) \int d^3x b_2(\vec{x}, \vec{x}) \\ &+ \frac{E^{-3/2}}{\Gamma(-1/2)} \int d^3x a_2(\vec{x}, \vec{x}) + \dots \end{aligned}$$

For the ground state ($\beta \rightarrow \infty$), we now immediately get an asymptotic expansion of the energy-density functional. We first determine the density

$$(3.28) \quad \begin{aligned} n(\vec{x}) &= \frac{\Omega}{(2\pi)^3} \int dE \frac{\mathcal{G}(E)}{e^{\beta(E-E_F)} + 1} |\psi_E(\vec{x})|^2 \Big|_{\beta=\infty} \\ &= \frac{1}{3\pi^2} \varepsilon_F^{3/2} + \frac{b_1(\vec{x}, \vec{x})}{4\pi^{3/2}} \varepsilon_F + \frac{a_1(\vec{x}, \vec{x})}{2\pi^2} \varepsilon_F^{1/2} + \\ &+ \frac{b_2(\vec{x}, \vec{x})}{4\pi^{3/2}} + \frac{a_2(\vec{x}, \vec{x})}{4\pi^2} \varepsilon_F^{-1/2} + \dots \end{aligned}$$

and the local energy density

$$\begin{aligned}
 \mathcal{U}(\vec{x}) &:= \frac{\Omega}{(2\pi)^3} \int dE \frac{f(E) \cdot E}{e^{\beta(E-\varepsilon_F)} + 1} |\psi_E(\vec{x})|^2 \Big|_{\beta=\infty} \\
 &= \frac{1}{5\pi^2} \varepsilon_F^{5/2} + \frac{b_1(\vec{x}, \vec{x})}{8\pi^{3/2}} \varepsilon_F^2 + \frac{a_1(\vec{x}, \vec{x})}{6\pi^2} \varepsilon_F^{3/2} \\
 &\quad - \frac{a_2(\vec{x}, \vec{x})}{4\pi^2} \varepsilon_F^{1/2} + \dots
 \end{aligned}
 \tag{3.29}$$

Eliminating the Fermi energy ε_F and integrating over the volume Ω we finally obtain the asymptotic expansion of the energy density functional

$$\begin{aligned}
 \mathcal{U}[n] &= \int d^3x \left\{ \frac{(3\pi^2)^{5/3}}{5\pi^2} n^{5/3}(\vec{x}) - \frac{(3\pi^2)^{4/3}}{8\pi^{3/2}} b_1(\vec{x}, \vec{x}) n^{4/3}(\vec{x}) \right. \\
 &\quad + \left(\mu_0(\vec{x}) - \frac{3\pi}{16} b_1^2(\vec{x}, \vec{x}) \right) n(\vec{x}) \\
 &\quad + \left(\frac{3\pi^{3/2} \cdot (3\pi^2)^{5/3}}{64} b_1^2(\vec{x}, \vec{x}) - \frac{(3\pi^2)^{5/3}}{4} 3\pi^{1/2} b_2(\vec{x}, \vec{x}) \right) n^{2/3}(\vec{x}) \\
 &\quad \left. + \dots \right\}.
 \end{aligned}
 \tag{3.30}$$

The interesting point is here, that our method of deriving Thomas-Fermi type expansion allows for a systematic study of surface effects. In particular, it is easily seen that non-surface terms, i.e. the only terms appearing in (3.24) if only compact manifolds without boundary are considered, yield an expansion of $\mathcal{U}[n]$ in terms of falling powers

of $n^{2/3}$; $n^{1/3}$ -terms in between these powers are solely determined by surface terms; for instance, the leading $n^{4/3}(\vec{x})$ correction to the kinetic energy term is a pure boundary term.

For finite temperatures, the grand canonical potential K is constructed as a density functional again by eliminating the Fermi energy ϵ_F following well known textbook methods. We now turn to our main problem:

b) Thomas-Fermi type expansions for the g -Hartree functional at $g=g_0$.

To determine the spectral density $\rho^{(E)}$ employing (3.26) and (3.24), we have to start from the g -Hartree equation for $g=g_0$, where we assume, for the time being, g_0 to be a given functional, e.g. by empirical considerations. Needless to say, g_0 determined by (2.26) has itself to be expanded in terms of the density to achieve a systematic construction of $\mathcal{U}[n]$ or $\tilde{K}[n]$. Instead of (3.22) we now have

$$(3.31) \quad (-\Delta + \mu_0(\vec{x}) + \mathcal{V}_{g_0}(\vec{x})) \psi_E(\vec{x}) = E \psi_E(\vec{x}).$$

Since (note that $n(\vec{x})$ denotes the quasiparticle density)

$$(3.32) \quad \mathcal{V}_{g_0}(\vec{x}) = g_0 \int d^3x' V(\vec{x}, \vec{x}') n(\vec{x}') + \text{Exchange term}$$

the simple minded insertion of $\mu_0(\vec{x}) + \mathcal{V}_{g_0}(\vec{x})$ into the asymptotic expansion (3.24), (3.27) and (3.30) seems to lead to an expansion in terms of ascending powers of $n^{1/3}(\vec{x})$, contrary to the original concepts of Thomas-Fermi theory. Indeed an interesting stability problem arises at this place which needs some further discussion. To be definite let us consider the case of a neutral atom: $N=Z$, where Z appears as a natural scaling parameter (the following discussion holds a fortiori

true for positively charged atoms $N \leq Z$). With $\mu_0(\vec{x})$ as the nuclear Coulomb potential

$$\mu_0(\vec{x}) = -\frac{Ze^2}{r}$$

we then have for the total potential to be used in the heat kernel expansion (3.24)

$$(3.33) \quad V_{\text{tot}}(\vec{x}) = \mu_0(\vec{x}) + U_{g_0}(\vec{x}) = -\frac{Ze^2}{r} (1-g_0) + \tilde{V}_d(\vec{x}) + (1-g_0) \tilde{V}_{\text{exch}}(\vec{x})$$

where $\tilde{V}_d(\vec{x})$ vanishes exponentially with the spatial extension of the atom as the scale and $\tilde{V}_{\text{exch}}$ is the exchange potential. It is the incomplete screening which results as an essential feature in the g-Hartree method that stabilises the asymptotic Thomas-Fermi expansions and finally, contrary to naive expectations, leads to an asymptotic series of decreasing powers of $n^{1/3}$. We shall see later that

$$1-g_0 = O(Z^{-1/3})$$

for large Z or

$$1-g_0 = O(n^{-1/3}(\vec{x}));$$

furthermore, $\tilde{V}_d(\vec{x})$ and $(1-g_0) \tilde{V}_{\text{exch}}$ in (3.33) are easily seen to contribute at most Z^0 . The leading term in $V_{\text{tot}}(\vec{x})$ is, therefore, of the order $Z^{4/3} O(n^{-1/3} [Z^{-1/3} x]) r^{-1}$ in the Thomas-Fermi scaling limit (see below) and our heat kernel expansion indeed leads to a Thomas-Fermi type series.

Turning our attention to the ground state and using (3.24) we find ($J_1(s)$ is the first Bessel function)

$$\begin{aligned}
 \sum_{\alpha} n_{\alpha} \psi_{\alpha}(\vec{x}) \psi_{\alpha}^*(\vec{y}) \Big|_{\beta=\infty} &= : P_{ex}(\vec{x}, \vec{y}) \\
 &= \frac{1}{\pi^2} \frac{\sin \sqrt{\epsilon_F} |\vec{x} - \vec{y}| - \sqrt{\epsilon_F} |\vec{x} - \vec{y}| \cos \sqrt{\epsilon_F} |\vec{x} - \vec{y}|}{|\vec{x} - \vec{y}|^3} \\
 (3.34) \quad &+ \frac{a_1(\vec{x}, \vec{y})}{2\pi^2} \cdot \frac{\sin \sqrt{\epsilon_F} |\vec{x} - \vec{y}|}{|\vec{x} - \vec{y}|} \\
 &+ \frac{b_1(\vec{x}, \vec{y}) \sqrt{\epsilon_F}}{2\pi^{3/2} |\vec{x} - \vec{y}|} J_1(\sqrt{\epsilon_F} |\vec{x} - \vec{y}|) + \dots
 \end{aligned}$$

and, from that, the exchange contribution to the energy functional

$$(3.35) \quad \mathcal{U}_{exch} = - \frac{(1-g)}{2} \cdot \frac{1}{2} \cdot \int d^3x \int d^3x' \frac{P_{ex}(\vec{x}, \vec{x}') P_{ex}(\vec{x}', \vec{x})}{|\vec{x} - \vec{x}'|}.$$

A straightforward calculation leads to

$$(3.36) \quad \mathcal{U}_{exch}[n] = A_1 + A_2 + A_3 + \dots$$

with

$$A_1 = - (1-g) \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int d^3x n^{4/3}(\vec{x})$$

$$A_2 = -(1-g) \cdot \pi \int d^3x \int d^3x' \frac{\rho_1^2(\vec{x}, \vec{x}')}{4\pi^3 |\vec{x} - \vec{x}'|^3} \cdot n^{1/3}(\vec{x}) \cdot \int_1^2 (n^{1/3}(\vec{x}) |\vec{x} - \vec{x}'|)$$

$$A_3 = -(1-g) \cdot \pi \cdot \int d^3x \int d^3x' \frac{\alpha_1(\vec{x}, \vec{x}')}{|\vec{x} - \vec{x}'|^5} \cdot \frac{1}{\pi^4} \cdot \sin(|\vec{x} - \vec{x}'| \cdot n^{1/3}(\vec{x})).$$

$$\cdot \left\{ \sin(|\vec{x} - \vec{x}'| \cdot n^{1/3}(\vec{x})) - n^{1/3}(\vec{x}) \cdot |\vec{x} - \vec{x}'| \cdot \cos(|\vec{x} - \vec{x}'| \cdot n^{1/3}(\vec{x})) \right\};$$

inserting¹⁴⁾ (V_{tot} is defined in (3.33))

$$\alpha_1(\vec{x}, \vec{y}) = -\frac{1}{|\vec{x} - \vec{y}|} \int d^3z \left(\frac{(\vec{x} - \vec{z})(\vec{z} - \vec{y})}{4\pi |\vec{x} - \vec{z}|^3} + \frac{1}{4\pi |\vec{y} - \vec{z}|} \right) \frac{V_{\text{tot}}(\vec{z})}{|\vec{y} - \vec{z}|}$$

$$(3.37) \quad b_1(\vec{x}, \vec{y}) = -\frac{(4\pi)^{3/2}}{8\pi} R^2 \delta(|\vec{x}| + |\vec{y}| - 2R) \int_{S_2} d^2\mathcal{J} e^{i\mathcal{J} \cdot (\hat{x} - \hat{y})}$$

where S_2 is the unit two-sphere and $\hat{x}, \hat{y}$ are unit vectors, we get an explicit yet complicated expression for the functional $\mathcal{U}_{\text{exch}}[n]$. In a local density approximation (LDA) which we obtain from a short-distance expansion of the integrands in (3.36) the assembled energy-density functional finally reads

$$(3.38) \quad \mathcal{U}_{\text{LDA}}[n] = \int d^3x \left\{ c_0 n^{5/3}(\vec{x}) + c_1 n^{4/3}(\vec{x}) + c_2 n(\vec{x}) + c_3 n^{2/3}(\vec{x}) + \frac{g}{2} \int d^3x' \frac{n(\vec{x})n(\vec{x}')}{|\vec{x} - \vec{x}'|} + \dots \right\}$$

with

$$C_2 = \frac{(3\pi^2)^{5/3}}{5\pi^2}$$

$$C_1 = -\frac{R^2}{8\pi^{3/2}} \cdot (3\pi^2)^{4/3} S(|\vec{x}| - R) - (1-g)^{3/4} \left(\frac{3}{\pi}\right)^{1/3}$$

$$C_2 = -a_1(\vec{x}, \vec{x}) - \frac{3\pi}{16} b_1^2(\vec{x}, \vec{x}) - (1-g)^{1/4} \frac{1}{4\sqrt{\pi}} b_1(\vec{x}, \vec{x})$$

$$C_3 = -\frac{(1-g)}{2\pi^3} (3\pi^2)^{2/3} a_1(\vec{x}, \vec{x}) - (1-g) b_1^2 \frac{(3\pi^2)^{2/3}}{4\pi^2} \cdot \frac{3}{4},$$

where $a_1(\vec{x}, \vec{x})$ etc. are obtained from (3.25) by replacing $\mu_0(\vec{x}) \rightarrow V_{\text{tot}}(\vec{x})$ or directly from (3.27).

Needless to say, higher terms can be obtained with this method by further systematic expansion.

We now turn to a discussion of Thomas-Fermi type expansions of the functional g_0 where, again, we consider explicitly only the ground state. According to (2.26) g_0 is to be determined from $(1-g_0 = \gamma_0)$

$$\ln Z^{\text{cor}} = -\frac{g_0}{2} \text{ (diagram with wavy line) } - \frac{\gamma_0}{2} \text{ (diagram with straight line) } -$$

(3.39)

$$- \frac{g_0^2}{2} \text{ (diagram with two wavy lines) } + g_0 \gamma_0 \text{ (diagram with wavy and straight lines) } -$$

$$- \frac{\gamma_0^2}{2} \text{ (diagram with two straight lines) } + \dots \stackrel{!}{=} 0$$

The Feynman rules have been given in chapter 2 and ref.(4), here we retain only the following features; the n-th order graphs contains (n-1) factors $(k_i^2 - k_j^2)^{-1}$; between two vertices each fermionic line (straight lines) carries an index α which is to be summed from threshold to the Fermi-energy ϵ_F or from ϵ_F to infinity. Hence, in the Thomas-Fermi limit, we have to insert $P_{\alpha\alpha}(\vec{x}, \vec{x}')$ or $\delta(\vec{x} - \vec{x}') - P_{\alpha\alpha}(\vec{x}, \vec{x}')$ using the asymptotic expansion (3.34) and then integrate over all vertices. An asymptotic expansion in terms of ϵ_F is obtained in this manner (the expansion parameter is, of course,

$$(\text{mean potential energy})/\epsilon_F$$

as it is in (3.27) to (3.29)) from which, eliminating ϵ_F with the help of (3.28), we gain the functional we are looking for:

$$(3.40) \quad g_0 = \tilde{g}_0[n(\vec{x}); \beta, \Omega]$$

which will considerably simplify if LDA is used.

In order to formulate our main point in this context we do not need to write down the Thomas-Fermi expansion of $\tilde{g}_0$ explicitly, it suffices to consider the relevant scaling limit

$$\begin{aligned} N/2 &= \text{const.} \leq 1 \\ Z &\rightarrow \infty \end{aligned}$$

which is achieved by scaling

$$(3.41) \quad \begin{aligned} \vec{x} &\rightarrow Z^{-1/3} \cdot \vec{x} \\ E &\rightarrow Z^{4/3} \cdot E \end{aligned}$$

The graphs (3.39) are composed of integrals

$$\langle \alpha \beta | V | \gamma \delta \rangle := \int d^3x \int d^3x' \psi_\alpha^*(\vec{x}) \psi_\beta(\vec{x}) \frac{e^2}{|\vec{x} - \vec{x}'|} \psi_\gamma^*(\vec{x}') \psi_\delta(\vec{x}'),$$

where, for the sake of determining the leading asymptotic term in Z , the $\psi_\alpha(\vec{x})$ can be replaced by plane waves

$$\psi_\alpha(\vec{x}) \rightarrow \frac{1}{\sqrt{\Omega}} e^{i \vec{k}_\alpha \cdot \vec{x}}.$$

Introducing the normalised vectors $\hat{x} = L|\vec{x}|$ and $\hat{k} = k_F^{-1} \cdot k$ ($\epsilon_F = k_F^2$, $L = \Omega^{1/3}$) we have

$$\begin{aligned} \langle \alpha \beta | V | \gamma \delta \rangle &= \frac{1}{L} \int d\hat{x}_1 \int d\hat{x}_2 \cdot \frac{e^{-i\mathcal{G}(\hat{k}\hat{x}_1 + \hat{k}'\hat{x}_2)}}{|\hat{x}_1 - \hat{x}_2|} \\ (3.42) \quad &= \frac{1}{L} \int_0^1 r_1^2 dr_1 \int_0^1 r_2^2 dr_2 \sum_{l=0}^{\infty} (-1)^l P_l(\cos \Theta_{\hat{k}\hat{k}'}) j_l(\mathcal{G} \cdot y_1) j_l(\mathcal{G} \cdot y_2) \end{aligned}$$

with

$$\begin{aligned} \mathcal{G} &= k_F \cdot L \\ \hat{k} &= k_\alpha - k_\beta ; \quad \hat{k}' = k_\gamma - k_\delta \\ y_1 &= r_1 \cdot |\hat{k}| ; \quad y_2 = r_2 \cdot |\hat{k}'|. \end{aligned}$$

In the scaling limit (3.41) we find with

$$\mathcal{G} \rightarrow z^{1/3} \cdot \mathcal{G}$$

$$\begin{aligned}
 \langle \alpha \beta | V | \delta \gamma \rangle &\sim Z^{-1/3} && \text{for } \alpha \neq \beta; \delta \neq \gamma \\
 \langle \alpha \alpha | V | \delta \gamma \rangle &\sim Z^0 && \text{for } \delta \neq \gamma \\
 \langle \alpha \alpha | V | \beta \beta \rangle &\sim Z^{1/3}
 \end{aligned}
 \tag{3.43}$$

The asymptotic behaviour shows an oscillatory behaviour which, by (3.39), qualitatively speaking, yields an oscillatory behaviour of g_0 . Indications of the latter can be seen¹⁵⁾ in empirical determinations of g_0 .

Determining now the leading power behaviour of a n -th order graph Γ_n the difference, seen in (3.43), between tadpole and non-tadpole graphs is essential (n_t is the number of tadpoles in Γ_n)

$$\begin{aligned}
 \Gamma_n &\sim Z^{2n} (Z^{-4/3})^{n-1} \cdot (Z^{-1/3})^{n-n_t} \\
 &= Z^{\frac{1}{3}(n+n_t+4)};
 \end{aligned}
 \tag{3.44}$$

in deriving this formula we used the fact that in calculating Γ_n $2n$ phase-space integrations, $n-1$ "retardation" factors $(k_i^2 - k_j^2)^{-1}$ and n integrals (3.43) have to be included.

The leading power obtains from the graph with the maximal number of tadpoles at fixed order. Thus, if we now turn to the calculation of g_0 to m -th order of perturbation theory, (3.39) written in successive order in Z now reads as (the c_m are irrelevant statistical factors)

$$\gamma_0^m \cdot \text{[diagram with } m \text{ tadpoles]} + \gamma_0^{m-1} g_0 c_{m-1} \text{[diagram with } m-1 \text{ tadpoles]} + \dots = 0
 \tag{3.45}$$

which upon scaling $\gamma_0 = \tilde{\gamma}_0 \bar{z}^{-1/3}$ turns into an equation

$$f_1(\tilde{\gamma}_0) \cdot \bar{z}^{1/3(m+4)} + O(\bar{z}^{1/3(m+3)}) = 0$$

and

$$f_1(\tilde{\gamma}_0) = 0$$

fixes $\tilde{\gamma}_0$. Hence, to any order m

$$(3.46) \quad g_0 = 1 - \tilde{\gamma}_0 \bar{z}^{-1/3} + O(\bar{z}^{-2/3}),$$

the higher order terms $O(\bar{z}^{-2/3})$ have to be determined by an analogous procedure.

The graphs in (3.45) are incorporated to leading order in Z which, pictorially speaking, is given as the leading short distance term. This however, factorises such that the dependence of $\tilde{\gamma}_0$ on the order m in which it is calculated approximately disappears.

Seen from the point of view of Thomas-Fermi theory the essential mechanism of the g -Hartree method now appears: the tadpole structure of the perturbative expansion of $\ln Z^{\text{cov}}$ (which essentially parametrises the lack of normal ordering in functional methods) induces a dominant Z -behaviour. The latter is compensated by decreasing powers of Z in g_0 to such a degree that the total correlation energy is made to vanish. Considered as a functional, the asymptotic expansion (3.46) translates into an expansion of $\tilde{\gamma}_0$ [(3.40)] in terms of power of $n^{1/3}(z)$. Thus,

the total energy or the grand canonical potential $\mathcal{K}$ is written as an expansion in terms of decreasing powers of $n^{1/3}(\vec{r})$ where $n(\vec{r})$, notably, is the quasiparticle density connected to the observable density by (3.8): the g-Hartree method gives an algorithm to compute the coefficients of this expansion in terms of the fundamental parameters defined in the action of our system.

5. Conclusions

Thermodynamic properties of the electrically neutral inhomogeneous electron gas were studied within the framework of the g-Hartree approach. It is shown that for the choices (2.26) and (3.14) the exact grand canonical potential has the form (1.2i) and (1.2ii), respectively and, therefore, closely resembles the potential for the free fermion gas. Hence, the g-Hartree spectra defined by (2.19) with g given by (2.26) or (3.14) can be visualised as quasiparticle spectra introduced¹⁾ by Landau in his theory of Fermi liquids. The temperature dependence of these g-Hartree spectra is determined by the Fermi distribution in (2.19) and the free fermion gas analogy holds in a wide temperature range limited only by eventually occurring singularities.

The quasiparticle interpretation then serves us as the conceptual background for deriving a functional series for the total energy of the ground state (or the grand canonical potential) in terms of the quasiparticle density which is asymptotic in the Thomas-Fermi limit. This expansion is to be understood as a quantum field theoretic approximation scheme for a theory defined by its microscopic interactions, i.e. a Lagrangian in terms of the relevant fields. The technique applied to get these asymptotic series relies on the Seeley expansion of the heat kernel for Schrödinger operators. The latter depends on the boundary of

the system's volume Ω and is well suited to facilitate the study of boundary effects.

Our treatment of the inhomogeneous electron gas has been non-relativistic although many of the derivations apply for the relativistic case as well. We shall report on this problem elsewhere.

A numerical study of our density functional (3.38) is under consideration. The results which show a substantial improvement for both the total energies and the density distribution will be published in a subsequent paper.

Appendix:

The determination of the partition function of a Fermi gas in a space-dependent chemical potential $\mu(\vec{x})$ (which simply acts as an external potential) requires the computation of fermionic determinants. We present the details of this calculation for time-independent and time-dependent external potentials.

We have to calculate the functional integral

$$(A.1) \quad Z = \int_{\text{antiperiodic}} \mathcal{D}\psi \int \mathcal{D}\psi^* e^{S[\psi, \psi^*]}$$

where

$$(A.2) \quad S[\psi, \psi^*] = \int_0^\beta d\tau \int_\Omega d^3x \psi^*(\vec{x}, \tau) (-\partial_\tau - \mathcal{D}) \psi(\vec{x}, \tau)$$

is the euclidean action for fermions interacting with an external potential $\mu(\vec{x})$

$$(A.3) \quad D = D_{\text{kin}} + \mu(\vec{x}),$$

D_{kin} is the non-relativistic or relativistic kinetic energy. To describe fermions at equilibrium in a volume Ω at temperature β^{-1} we have to integrate over antiperiodic electron field configurations

$$(A.4) \quad \psi(\vec{x}, \tau) = -\psi(\vec{x}, \tau + \beta),$$

the fields ψ are taken to be Grassmannian (anticommuting) in order to account for the fermionic character. Hence, in a formal sense, we have

$$(A.5) \quad \begin{aligned} Z &= N \cdot \det(-\partial_\tau - D) \\ &= Z[\mu(\vec{x}); \beta, \Omega], \end{aligned}$$

N is a normalisation factor and the (grand canonical) partition function Z results as a functional of the chemical potential $\mu(\vec{x})$ and a function of temperature and volume.

To implement the antiperiodic boundary conditions we decompose into modes

$$(A.6) \quad \psi(\vec{x}, \tau) = \frac{1}{\sqrt{\beta}} \sum_{m=-\infty}^{+\infty} \psi_m(\vec{x}) e^{-\frac{2\pi i}{\beta}(m + \frac{1}{2}) \cdot \tau}$$

and obtain

$$(A.7) \quad \mathbb{Z}/N = \pi \int \mathcal{D}\psi_m \int \mathcal{D}\psi_m^* e^{-\frac{1}{2} \int d^3x \psi_m^*(\vec{x}) \left(\frac{2\pi i}{\beta} (m + \frac{1}{2}) - \mathcal{D} \right) \psi_m(\vec{x})}$$

Therefore,

$$(A.8) \quad \mathbb{Z}/N = \prod_m \det \left(\mathcal{D} - \frac{2\pi i}{\beta} (m + \frac{1}{2}) \right)$$

and

$$(A.9) \quad \ln \mathbb{Z}/N = \sum_{m=-\infty}^{+\infty} \text{tr} \ln \left(\mathcal{D} - \frac{2\pi i}{\beta} (m + \frac{1}{2}) \right).$$

The latter expression for $\ln \mathbb{Z}/N$ has to be considered as a formal series on which physically acceptable summation prescriptions have to be imposed. First of all we prescribe symmetric summation, i.e.

$$(A.10) \quad \begin{aligned} \ln \mathbb{Z}/N &= \text{tr} \ln \left(\mathcal{D} - \frac{i\pi}{\beta} \right) \\ &+ \sum_{m=1}^{\infty} \text{tr} \ln \left\{ \left(\mathcal{D} - \frac{i\pi}{\beta} \right)^2 + \left(\frac{2\pi m}{\beta} \right)^2 \right\}. \end{aligned}$$

Note that the logarithms under the sum stay on the first sheet since

$$(A.11) \quad \arg \left[\left(D - \frac{i\pi}{\beta} \right)^2 + \left(\frac{2\pi m}{\beta} \right)^2 \right] < 45^\circ$$

$$(0 \leq \beta \leq \infty),$$

the first term in (A.10) needs special consideration as we shall see in a moment.

The sum is performed by using ζ -function regularisation¹⁵⁾. Abbreviating

$$\lambda_k := \left(\frac{2\pi k}{\beta} \right)^2 + \left(D - \frac{i\pi}{\beta} \right)^2,$$

the sum

$$\sum_{m=1}^{\infty} \ln \lambda_m$$

can be obtained in the following manner:

$$\text{Define } (\bar{D} := D - \frac{i\pi}{\beta})$$

$$(A.12) \quad \zeta(s, \bar{D}) := \sum_{m=1}^{\infty} \lambda_m^{-s}$$

then

$$(A.13) \quad \sum_{m=1}^{\infty} \ln \lambda_m := - \frac{d}{ds} \zeta(s, \bar{D}) \Big|_{s=0}$$

if $\zeta(s, \bar{D})$ can be shown to be regular at $s=0$.

To this end we write

$$(A.14) \quad \mathcal{Y}(s, \bar{D}) = \frac{1}{\Gamma(s)} \int_0^\infty dt \, t^{s-1} e^{-\bar{D}^2 t} \sum_{m=1}^\infty e^{-\left(\frac{2\pi m}{\beta}\right)^2 t}$$

where we used

$$\lambda_n^{-s} = \frac{1}{\Gamma(s)} \int_0^\infty dt \, t^{s-1} e^{-\lambda_n \cdot t}$$

From (A.11) we conclude that singularities in s of $\mathcal{Y}(s, \bar{D})$ are generated at the lower integration bound. To extract these singularities explicitly we employ¹⁶⁾

$$\frac{\beta}{2\sqrt{\pi t}} \sum_{m=-\infty}^{+\infty} e^{-\frac{\beta^2 m^2}{4t}} = \sum_{m=-\infty}^{+\infty} e^{-\left(\frac{2\pi m}{\beta}\right)^2 t}$$

and arrive at

$$(A.15) \quad \begin{aligned} \mathcal{Y}(s, \bar{D}) = & \beta \bar{D}^{-2s+1} \frac{\Gamma(s-\frac{1}{2})}{4\sqrt{\pi} \Gamma(s)} - \frac{1}{2} \bar{D}^{-2s} \\ & + \frac{\beta}{\sqrt{\pi} \Gamma(s)} \bar{D}^{-2s+1} \sum_{m=1}^\infty \left(\frac{m\beta\bar{D}}{2}\right)^{s-\frac{1}{2}} \cdot K_{\frac{1}{2}-s}(m\beta\bar{D}), \end{aligned}$$

an expression which is regular at $s=0$.

The sum $\sum \ln \lambda_m$ as defined in (A.13) is then computed to be

$$(A.16) \quad \sum_{m=1}^\infty \ln \lambda_m = \frac{1}{2} \beta \bar{D} - \ln \bar{D} - \ln(1 + e^{-\beta \bar{D}}).$$

Hence,

$$(A.17) \quad \ln \frac{Z}{N} = + \frac{1}{2} \text{tr} \beta \bar{D} - \text{tr} \ln (1 + e^{-\beta D}).$$

The first term in this formula needs further consideration. Introducing the spectrum of $D = D_{\text{kin}} + \mu(\vec{x})$

$$(A.18) \quad D \psi_\alpha(\vec{x}) = \varepsilon_\alpha \psi_\alpha(\vec{x}),$$

ψ_α normalised to unity, the term $\frac{\beta}{2} \text{tr} D$ is seen to be the familiar vacuum contribution

$$(A.19) \quad \frac{1}{2} \text{tr} \beta D = \sum_\alpha \frac{\beta \varepsilon_\alpha}{2}$$

which can be omitted unless there are non-trivial zero modes in (A.18).

To see this observe that

$$\frac{\delta}{\delta \mu(\vec{x})} \sum_\alpha \varepsilon_\alpha \Big|_{\mu_0(\vec{x})} = \sum_\alpha |\psi_\alpha(\vec{x})|^2 = \delta(0)$$

where the last equation holds, independently of $\mu_0(\vec{x})$, if there are no non-trivial zero modes. Hence, $\sum \varepsilon_\alpha$ does not contribute to the equation of state and is irrelevant for the equilibrium properties of our system.

There is yet another term in (A.17), $-\frac{1}{2} \text{tr}(i\pi)$, which corresponds to a temperature independent phase factor in Z and which we absorb into the normalisation factor. Phase factors of this kind typically appear in functional determinants of fermionic systems.

Thus we finally get

$$\begin{aligned}
 \ln Z &= - \text{tr} \ln (1 + e^{-\beta D}) \\
 &= - \sum_{\alpha} \ln (1 + e^{-\beta \epsilon_{\alpha}}),
 \end{aligned}
 \tag{A.20}$$

a familiar expression indeed.

Next, we have to generalise our considerations to the case of time-dependent, periodic potentials ("time" means, of course, purely imaginary euclidean time), i.e.

$$D \longrightarrow D_p = D + \mathcal{V}(\vec{x}, \tau)
 \tag{A.21}$$

where

$$\mathcal{V}(\vec{x}, \tau) = \mathcal{V}(\vec{x}, \tau + \beta).
 \tag{A.22}$$

To compute $\det(-\partial_{\tau} - D_p)$ we start by defining the spectrum of the Wick-rotated operator

$$(i\partial_t - \tilde{D}_p) \Psi_m(\vec{x}, t) = -\tilde{\epsilon}_m(T) \Psi_m(\vec{x}, t)
 \tag{A.23}$$

where the Wick rotation

$$\begin{aligned}
 \tau &\longrightarrow +it \\
 \beta &\longrightarrow +iT
 \end{aligned}
 \tag{A.24}$$

induces

$$D_p \rightarrow \tilde{D}_p = D + \check{\mathcal{Y}}(\vec{x}, t)$$

and $\check{\mathcal{Y}}$ is periodic in t with period T . Periodicity leads to a Bloch ansatz

$$(A.25) \quad \psi_{k\alpha}(\vec{x}, t) = e^{ik t} \mu_{k\alpha}(\vec{x}, t)$$

and

$$(A.26) \quad \mu_{k\alpha}(\vec{x}, t) = \mu_{k\alpha}(\vec{x}, t + T).$$

The fermion field $\psi_{k\alpha}$ has to be antisymmetric, thus

$$(A.27) \quad k = \frac{2\pi}{T} \left(m + \frac{1}{2}\right) \quad m = 0, \pm 1, \dots$$

The spectrum, therefore, has the following structure

$$(A.28) \quad \tilde{\varepsilon}_{m\alpha} = \frac{2\pi}{T} \left(m + \frac{1}{2}\right) + \tilde{\varepsilon}_{\alpha}$$

with

$$(A.29) \quad (i\partial_t - \tilde{D}_p) \mu_{0\alpha}(\vec{x}, t) = -\tilde{\varepsilon}_{\alpha}(T) \mu_{0\alpha}(\vec{x}, t).$$

A derivation which almost literally follows the deductions leading from (A.1) to (A.20) (traces have to be performed in the first Brillouin zone defined in (A.29)) finally leads to

$$(A.30) \quad \ln Z = - \sum_{\alpha} \ln (1 + e^{-\beta \epsilon_{\alpha}(\beta)});$$

writing $\ln Z$ in this way we implied a Wick rotation back into the euclidean region

$$(A.31) \quad \tilde{\epsilon}_{\alpha}(T) \longrightarrow \epsilon_{\alpha}(\beta).$$

Since $i\partial_t - \tilde{D}_{\rho}$ is hermitian ($\tilde{\psi}$ is assumed to be real!), the $\tilde{\epsilon}_{\alpha}(T)$ are real which is no longer necessarily true for $\epsilon_{\alpha}(\beta)$.

An attempt to treat fermionic determinants with time-dependent periodic potentials can already be found in ref.(18), an erroneous restriction to the lowest Brillouin zone led, however, to an incorrect result.

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