

Relativistic Density Functional Theory

E. Engel and R. M. Dreizler

Institut für Theoretische Physik, Universität Frankfurt, Robert Mayer Str. 8-10,
60054 Frankfurt/Main, Germany

Summary. An overview of relativistic density functional theory covering its foundations, the construction of explicit functionals and applications to spherical atoms is given. After a brief summary of the relevant field theoretical background we discuss the Hohenberg-Kohn theorem for quantum electrodynamical systems as well as the corresponding Kohn-Sham equations, emphasising in particular the renormalisation of ground state energies and currents required. We then outline the transition from the full quantum electrodynamical Kohn-Sham equations to the more practical variants which are actually used in applications. As an extension of the Kohn-Sham equations we also summarise the relativistic optimised-potential-method (OPM) which, in addition to the kinetic energy, also treats the exchange energy on the basis of Kohn-Sham orbitals. As far as the construction of explicit functionals is concerned, we review the local density approximation (LDA) and the weighted density approximation (WDA) for the exchange-correlation energy as well as the gradient expansion of the kinetic energy, again addressing in detail questions of renormalisation. The relativistic corrections to the ground state, single particle and exchange energies as well as exchange potentials of atoms are then examined within the exchange-only limit of the no-sea approximation to the full relativistic Kohn-Sham equations, comparing the LDA and the WDA with the results obtained by the relativistic OPM. In addition, we investigate transverse exchange and correlation contributions within the LDA by comparison with quantum chemical data.

1. Introduction

Density functional theory (DFT) of nonrelativistic many particle systems has progressed steadily over the last thirty years, so that it is now able to compete successfully with more traditional many body techniques, as e.g. configuration interaction (CI) methods, for the *ab initio* determination of *ground state* properties [1, 2, 3, 4]. The CI approach involves a rather straightforward concept, whose application is, however, limited by technical aspects (computer speed and memory) to systems with modest particle numbers. In the DF approach the first task is to find a sufficiently accurate representation of the ground state energy and other ground state observables as functionals of the ground state density. If such a representation is available (at least for a wider class of systems as e.g. finite Coulomb systems) further application is much simpler and can be carried through for larger systems.

For the application of DFT two avenues are possible. The first is the exploitation of a direct variational principle [5] with the density (or some suitable extension as spin-up and spin-down densities) as the basic variational variable. With this approach, usually referred to as extended Thomas-Fermi (ETF) models, no results of high accuracy have been obtained. The second,

the Kohn-Sham (KS) scheme [6], relies on a representation of the density in terms of single particle orbitals. In this sense it is akin to the Hartree-Fock (HF) approach. The difference is, however, that the KS orbitals experience a local (i.e. multiplicative) single-particle potential, which also includes correlation effects (at least to some degree, depending on the state of art). In the last years rather refined approximations for this potential have been developed (as e.g. generalised gradient approximations — GGAs), which yielded among others results that compared favourably with conventional many-body methods in recent comparative studies for a variety of small molecules [2, 3].

These quantum chemical studies were restricted to rather light elements [2, 3], so that relativistic effects did not play any role. However, as soon as heavier atoms are involved (with Au being the prime candidate) they become essential for understanding the physical and chemical properties of atoms and molecules. Beyond the well known kinematic effects as the contraction or expansion of relativistic orbitals and the corresponding bond length modifications in molecules, also the nonadditivity of relativistic and exchange-correlation (xc) effects has recently been emphasised [7] (for a detailed account of the importance of relativity for chemical bonding we refer the reader to Refs.[8, 9]). Clearly, a DFT description of such high- Z systems also has to reflect their relativistic character, in particular, as even for atoms with moderate Z relativistic contributions to the xc-energy are larger than the differences between the most refined nonrelativistic xc-energy functionals [10, 11].

The development of a DF approach to relativistic many particle systems has, however, been much slower than that of its nonrelativistic counterpart, although a precursor of modern relativistic DFT in the form of the relativistic Thomas-Fermi (TF) model [12, 13] was established with only a minor time delay with respect to the nonrelativistic TF approach [14, 15]. This and quite a number of subsequent attempts to incorporate relativity in explicit density functionals [16] were based on the first quantised Dirac equation, which is not an appropriate basis for the discussion of the full scale of relativistic effects in many particle systems. If one wishes to address photon retardation effects and antiparticle contributions besides the relativistic kinematics of the electrons the correct basis for the discussion of many electron systems is quantum electrodynamics (QED). A comparison of the general structure (and in particular of the diagrammatic formulation) of QED and of nonrelativistic many body theory reveals definite similarities, but the elimination of infinite zero point energies, the renormalisation of ultraviolet (UV) divergencies as well as the spinor and tensor structure of the quantities involved introduces substantial complications in the former case. These additional features are reflected in relativistic DFT (RDFT), both on the more formal level and in the derivation of explicit functionals. An extension of the Hohenberg-Kohn (HK) theorem [5] to the relativistic domain has first been formulated by Rajagopal and Callaway [17], showing that in a fully relativistic DF formalism the four current plays the role of the density as the basic DF variable.

The corresponding KS-equations have been given by Rajagopal [18] and independently by MacDonald and Vosko [19]. These authors mainly focussed on the Dirac structure of the relativistic KS (RKS) equations (including the four component form of the xc-potential) and the retardation corrections to the Coulomb interaction, but essentially neglected the fundamental questions related to radiative corrections. UV-divergencies first showed up in the RDFT context in the derivation of gradient corrections to the kinetic energy [16, 20, 21], but only very recently an attempt has been made [22] to explicitly deal with the issue of UV-renormalisation in the context of the relativistic HK-theorem and the RKS-equations. As a consequence of the complicated structure of the RKS-equations applications beyond their most simple version, the Dirac-Fock-Slater (DFS) approach [23] or its extensions [24], in which all relativistic effects in the xc-energy (as well as all radiative corrections) are neglected, are rare (compare Section 5.).

In this review we attempt to give a summary of the still restricted knowledge of RDFT for Coulomb systems (for an earlier review see [25]). Activity in the field of hadronic physics is not covered (we refer the interested reader to the relevant section in [22]). We begin with an outline of the background material in Section 2., but have chosen to relegate nearly all details into the Appendices. The foundations of RDFT, i.e. the HK-theorem, the KS-scheme, its extension in the form of the optimised potential method (OPM) and some remarks on the nonrelativistic limit, are addressed in Section 3.. We emphasise, in particular, practical aspects concerning the application of the relativistic KS-scheme. Explicit energy functionals for relativistic Coulomb systems are discussed in Section 4., where we outline the local density approximation (LDA) for exchange and, as far as they are known, for correlation contributions. In addition, we indicate first attempts to apply the weighted density approximation (WDA) in the relativistic regime. Results for the solution of the relativistic KS-equations for atoms are analysed in Section 5.. To our knowledge no corresponding results for molecules are yet available. Some concluding remarks indicating open problems and possible extensions (e.g. for thermal relativistic systems) are the contents of the final Section 6..

As indicated, we provide a more detailed summary of the background material for the discussion of RDFT in the Appendices. In particular, we address the question of perturbative renormalisation in vacuum quantum electrodynamics (Appendix A.), discuss the properties of the relativistic homogeneous electron gas (RHEG) (Appendix B.) in order to provide the input for the relativistic LDA (RLDA) and add some remarks on QED in the presence of external fields (Appendix C.). In addition, Appendix D. gives some information concerning the systematic derivation of inhomogeneity corrections to the RLDA, illustrating in particular the gradient expansion (GE) on the basis of linear response. Although we do not present relativistic ETF-results in this review, we briefly summarise (Appendix E.) the derivation of relativistic kinetic energy functionals via a semiclassical expansion of the electron prop-

agator as it demonstrates the occurrence and subsequent renormalisation of UV-divergencies in a transparent fashion.

We use $\hbar = c = 1$ throughout the manuscript (except for Section 3.4) and our metric is chosen as in Ref.[26], i.e. the space-time coordinates x are given by $x^\mu = (x^0 = t, \mathbf{x})$ with \mathbf{x} (or \mathbf{r}) being the usual position in space. Greek indices run from 0 to 3, Latin indices from 1 to 3. The summation convention is used throughout. The abbreviations used for the various functionals in this work are based on the following scheme: All relativistic functionals are labelled beginning with R (like RLDA for relativistic LDA), while their nonrelativistic counterparts start with NR. The same notation is used for the resulting computational schemes, e.g. NRLDA abbreviates results obtained by utilizing the nonrelativistic LDA functional in the non-relativistic KS-equations. The only exception to this rule is the Dirac-Fock-Slater approach (with $\alpha = 2/3$) characterised by DFS, which corresponds to the use of the nonrelativistic LDA for the exchange energy in the relativistic KS-equations. Finally, all differences between relativistic and nonrelativistic results are referenced by the generic name of the approximation, e.g. LDA.

2. Field Theoretical Background

An appropriate basis for a complete discussion of relativistic effects in many electron systems (atoms, molecules, clusters, solids) is quantum electrodynamics. In view of the large difference between the electron and the nuclear masses it is legitimate to treat the nuclei as fixed external sources¹. This standard approximation relies on the assumption of a common rest frame for all nuclei and thus partially breaks the covariance of the resulting many body theory. A system of Dirac particles, which interact by the exchange of photons and move in a given static external electromagnetic field $V^\mu(\mathbf{x})$ (representing the fixed nuclei — and additional fields if present) is characterised by a Lagrangian density of the form [27]

$$\mathcal{L}(x) = \mathcal{L}_e(x) + \mathcal{L}_\gamma(x) + \mathcal{L}_{int}(x) . \quad (2.1)$$

The three terms represent the free Dirac Lagrangian² of the fermions (electrons and positrons),

$$\mathcal{L}_e(x) = \frac{1}{4} \left\{ \left[\overleftarrow{\hat{\psi}}(x), (i\overleftarrow{\not{\partial}} - m)\hat{\psi}(x) \right] + \left[\hat{\overleftarrow{\psi}}(x)(-i\overleftarrow{\not{\partial}} - m), \hat{\psi}(x) \right] \right\} , \quad (2.2)$$

¹ In a truly covariant QED-approach to atoms and molecules both the nuclei and the electrons would have to be treated as dynamical degrees of freedom (at least on a classical level in the case of the nuclei).

² The vector bars on top of the partial derivatives indicate the direction in which the derivative has to be taken, i.e. in the second term of \mathcal{L}_e the partial derivatives act on $\hat{\overleftarrow{\psi}}(x)$.

the free photon Lagrangian,

$$\mathcal{L}_\gamma(x) = -\frac{1}{16\pi}\hat{F}_{\mu\nu}(x)\hat{F}^{\mu\nu}(x) - \frac{\lambda}{8\pi}(\partial_\nu\hat{A}^\nu(x))^2, \quad (2.3)$$

and the interaction term

$$\mathcal{L}_{int}(x) = -e\hat{j}^\nu(x)\left(\hat{A}_\nu(x) + V_\nu(\mathbf{x})\right). \quad (2.4)$$

The operators $\hat{\psi}(x)$ and $\hat{A}_\mu(x)$ are the fermion and photon field operators,

$$\hat{F}_{\mu\nu}(x) = \partial_\mu\hat{A}_\nu(x) - \partial_\nu\hat{A}_\mu(x), \quad (2.5)$$

and

$$\hat{j}^\nu(x) = \frac{1}{2}\left[\hat{\bar{\psi}}(x), \gamma^\nu\hat{\psi}(x)\right] \quad (2.6)$$

is the fermion four current operator. For the photon fields we have chosen to work in the covariant gauge so that we had to introduce the gauge fixing term [27, 26]

$$-\frac{\lambda}{8\pi}(\partial_\nu\hat{A}^\nu(x))^2$$

and to use the Gupta-Bleuler indefinite metric quantisation. For brevity we shall often restrict explicit formulae to some particular gauge, as e.g. the Feynman gauge $\lambda = 1$ or Landau gauge $\lambda = \infty$. For the external potential we use the gauge $\partial_i V^i(\mathbf{x}) = \nabla \cdot \mathbf{V}(\mathbf{x}) = 0$.

One of the most important properties of the Lagrangian (2.1) is its gauge invariance: A gauge transformation of the photon field,

$$\hat{A}_\nu(x) \rightarrow \hat{A}'_\nu(x) = \hat{A}_\nu(x) + \partial_\nu\Lambda(x) \quad ; \quad \partial_\mu\partial^\mu\Lambda(x) = 0, \quad (2.7)$$

can be absorbed by an accompanying phase transformation of the fermion field operator

$$\hat{\psi}(x) \rightarrow \hat{\psi}'(x) = \exp[-ie\Lambda(x)]\hat{\psi}(x), \quad (2.8)$$

leaving the Lagrangian (2.1) invariant,

$$\mathcal{L}(\hat{\psi}', \hat{A}') = \mathcal{L}(\hat{\psi}, \hat{A}). \quad (2.9)$$

On the other hand, due to the choice of a particular Lorentz frame the gauge invariance of \mathcal{L} with respect to gauge transformations of the external potential has been partially broken: Only static gauge transformations,

$$V'_\nu(\mathbf{x}) = V_\nu(\mathbf{x}) + \partial_\nu\Lambda(t, \mathbf{x}) \quad (2.10)$$

$$\hat{\psi}'(x) = \exp[-ie\Lambda(t, \mathbf{x})]\hat{\psi}(x) \quad (2.11)$$

$$\Lambda(t, \mathbf{x}) = Ct + \lambda(\mathbf{x}) \quad ; \quad \Delta\lambda(\mathbf{x}) = 0, \quad (2.12)$$

are admitted within the common rest frame of the nuclei. In addition to the Lagrangian the four current $\hat{j}^\mu(x)$, Eq.(2.6), is also invariant under the transformations (2.7,2.8) and (2.10-2.12).

Moreover, both the Lagrangian and the electronic four current have been written in a charge conjugation invariant form [27], i.e. under the charge conjugation $\hat{\mathcal{C}}$ (transforming electrons into positrons and vice versa) the four current (as a charge current rather than a probability current) changes its sign,

$$\hat{\mathcal{C}} \hat{j}^\nu(x) \hat{\mathcal{C}}^+ = -\hat{j}^\nu(x) \quad , \quad (2.13)$$

while in \mathcal{L} the fermion charge manifests itself in the coupling to external sources,

$$\hat{\mathcal{C}} \mathcal{L}[V^\nu] \hat{\mathcal{C}}^+ = \mathcal{L}[-V^\nu] \quad , \quad (2.14)$$

i.e. an external potential which attracts electrons repels positrons.

It is useful for the following discussion to consider the symmetries of the Lagrangian (2.1) in order to analyse the conservation laws of a system characterised by (2.1) on the most general level, i.e. without further specifying V^μ , and their consequences for the structure of a density functional approach to (2.1). We first consider continuous symmetries which in the field theoretical context are usually discussed on the basis of Noether's theorem (see e.g. [26, 28]). The most obvious symmetry of the Lagrangian (2.1), its gauge invariance (2.9), directly reflects current conservation,

$$\partial_\nu \hat{j}^\nu(x) = 0 \quad , \quad (2.15)$$

and thus conservation of the total charge,

$$\hat{Q} = \int d^3x \hat{j}^0(x) = \frac{1}{2} \int d^3x \left[\hat{\psi}^+(x), \hat{\psi}(x) \right] \quad . \quad (2.16)$$

As a consequence any ground state resulting from (2.1) can be classified with respect to its charge (but not particle number).

Energy and momentum conservation can be directly deduced from the 'continuity' equation for the energy momentum tensor³ [27, 28]. For the $\hat{T}^{\mu\nu}$ resulting from (2.1) one finds

$$\begin{aligned} \hat{T}^{\mu\nu}(x) &= \frac{i}{8} \left[\hat{\bar{\psi}}(x), \left(\gamma^\mu \bar{\partial}^\nu + \gamma^\nu \bar{\partial}^\mu - \gamma^\mu \bar{\partial}^\nu - \gamma^\nu \bar{\partial}^\mu \right) \hat{\psi}(x) \right] \quad (2.17) \\ &+ \frac{1}{4\pi} \left\{ \hat{F}^{\mu\rho}(x) \hat{F}_\rho{}^\nu(x) + \frac{1}{4} g^{\mu\nu} \hat{F}(x)^2 - \frac{\lambda}{2} g^{\mu\nu} \left(\partial_\rho \hat{A}^\rho(x) \right)^2 \right. \\ &\quad \left. - \lambda \left(\partial_\rho \partial_\tau \hat{A}^\tau(x) \right) \left(g^{\mu\nu} \hat{A}^\rho(x) - g^{\mu\rho} \hat{A}^\nu(x) - g^{\nu\rho} \hat{A}^\mu(x) \right) \right\} \\ &- \frac{e}{2} \left(\hat{j}^\mu(x) \hat{A}^\nu(x) + \hat{j}^\nu(x) \hat{A}^\mu(x) \right) \\ &+ \frac{e}{2} \left(\hat{j}^\mu(x) V^\nu(x) - \hat{j}^\nu(x) V^\mu(x) \right) \quad . \end{aligned}$$

³ We base our considerations on the 'symmetric' energy momentum tensor $\hat{T}^{\mu\nu}$ rather than the canonical $\hat{\Theta}^{\mu\nu}$. Both versions of the energy momentum tensor, of course, satisfy identical 'continuity' equations, i.e. all physical results are independent of this choice. $\hat{T}^{\mu\nu}$ represents a covariant combination of the energy, momentum and stress densities of the system.

From the last line of Eq.(2.17) it is obvious that, as we are dealing with an open system, the source field breaks the symmetry of $\hat{T}^{\mu\nu}$. As an immediate consequence $\hat{T}^{\mu\nu}$ does not satisfy a homogeneous 'continuity' equation but rather the external potential acts as a source of momentum,

$$\partial_\mu \hat{T}^{\mu\nu}(x) = e \hat{j}_\mu(x) \partial^\nu V^\mu(\mathbf{x}) \quad . \quad (2.18)$$

Only the zeroth component of the total four momentum, i.e. the energy, is conserved for general time-independent external potentials,

$$\partial_\mu \hat{T}^{\mu 0}(x) = 0 \quad \Rightarrow \quad \int d^3x \hat{T}^{00}(x) \text{ is conserved} \quad . \quad (2.19)$$

This implies that the system can be regarded as stationary in the common rest frame of the sources which allows an identification of the Hamiltonian,

$$\hat{H} \equiv \int d^3x \hat{T}^{00}(x) = \hat{H}_e + \hat{H}_\gamma + \hat{H}_{int} + \hat{H}_{ext} \quad (2.20)$$

$$\hat{H}_e = \frac{1}{2} \int d^3x \left[\hat{\psi}(x), \left(-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m \right) \hat{\psi}(x) \right] \quad (2.21)$$

$$\hat{H}_\gamma = -\frac{1}{8\pi} \int d^3x \left\{ \partial^0 \hat{A}_\nu(x) \partial^0 \hat{A}^\nu(x) + \boldsymbol{\nabla} \hat{A}_\nu(x) \cdot \boldsymbol{\nabla} \hat{A}^\nu(x) \right\} \quad (2.22)$$

$$\hat{H}_{int} = e \int d^3x \hat{j}^\mu(x) \hat{A}_\mu(x) \quad (2.23)$$

$$\hat{H}_{ext} = e \int d^3x \hat{j}^\mu(x) V_\mu(\mathbf{x}) \quad , \quad (2.24)$$

where we have chosen Feynman gauge, $\lambda = 1$, for simplicity. If, in addition, the potential is independent of one spatial coordinate the corresponding momentum is also conserved.

The discussion of angular momentum conservation is based on the generalised angular momentum tensor⁴ (compare [27, 28]),

$$\hat{j}^{\mu, \rho\tau} = \hat{j}_e^{\mu, \rho\tau} + \hat{j}_\gamma^{\mu, \rho\tau} \quad (2.25)$$

$$\hat{j}_e^{\mu, \rho\tau} = -\frac{1}{4} \left[\hat{\psi}, \left(i\gamma^\mu \left(x^\rho \bar{\partial}^\tau - \bar{\partial}^\tau x^\rho - x^\tau \bar{\partial}^\rho + \bar{\partial}^\rho x^\tau \right) + \left\{ \gamma^\mu, \frac{\sigma^{\rho\tau}}{2} \right\} \right) \hat{\psi} \right]$$

⁴ Here we have chosen to define the generalised angular momentum tensor via the canonical energy-momentum tensor $\Theta^{\mu\nu}$,

$$J^{\mu, \rho\tau} = \Theta^{\mu\rho} x^\tau - \Theta^{\mu\tau} x^\rho - \sum_{r,s} \frac{\partial \mathcal{L}}{\partial (\partial_\mu \phi_r)} S_{rs}^{\rho\tau} \phi_s \quad ,$$

where the $S_{rs}^{\rho\tau}$ characterise the transformation properties of the fields ϕ_s under Lorentz transformations [28], rather than via $T^{\mu\nu}$ in the form $M^{\mu, \rho\tau} = T^{\mu\rho} x^\tau - T^{\mu\tau} x^\rho$. Both tensors, of course, lead to identical continuity equations and conserved angular momenta.

$$\begin{aligned} \hat{J}_\gamma^{\mu,\rho\tau} &= \frac{1}{4\pi} \left(\hat{F}^{\mu\nu} + \lambda g^{\mu\nu} (\partial \cdot \hat{A}) \right) \left(x^\rho \partial^\tau \hat{A}_\nu - x^\tau \partial^\rho \hat{A}_\nu + g^\rho{}_\nu \hat{A}^\tau - g^\tau{}_\nu \hat{A}^\rho \right) \\ &\quad + \left(g^{\mu\tau} x^\rho - g^{\mu\rho} x^\tau \right) \mathcal{L}_\gamma \quad , \end{aligned}$$

which represents the angular momentum densities of both the fermions ($\hat{J}_e^{\mu,\rho\tau}$) and the photons ($\hat{J}_\gamma^{\mu,\rho\tau}$) in a covariant form. Eq.(2.25) explicitly demonstrates the coupling of spin and orbital angular momentum for both fermions and photons on the most general level. In analogy to Eq.(2.18) the external potential acts as a source of angular momentum in the 'continuity' equation for $\hat{J}^{\mu,\rho\tau}$,

$$\partial_\mu \hat{J}^{\mu,\rho\tau}(x) = e \hat{j}_\mu(x) \left(x^\tau \partial^\rho V^\mu(\mathbf{x}) - x^\rho \partial^\tau V^\mu(\mathbf{x}) + g^{\tau\mu} V^\rho(\mathbf{x}) - g^{\rho\mu} V^\tau(\mathbf{x}) \right) . \quad (2.26)$$

As for the linear momentum, in general no component of the angular momentum is conserved: As a fixed nuclear rest frame has been chosen no 'boost' momentum $\int d^3x \hat{J}^{0,0j}(x)$ can be conserved and the conservation of a conventional angular momentum component $\int d^3x \hat{J}^{0,ij}(x)$ requires specific spatial symmetries. For instance, if all spatial components V^j vanish and V^0 only depends on $(x^1)^2 + (x^2)^2$, i.e. for axially symmetric electrostatic potentials, one finds as expected that the angular momentum with respect to the x^3 -axis, $\int d^3x \hat{J}^{0,12}(x)$, is a conserved quantity.

As far as discrete symmetries are concerned three types are usually considered within QED [26, 29]:

- For parity to be a good quantum number some reflection symmetry of the potential is required (the same holds, of course, for more complex discrete spatial symmetries).
- As for the Lagrangian, charge conjugation is no symmetry of the Hamiltonian,

$$\hat{C} \hat{H}[V^\nu] \hat{C}^+ = \hat{H}[-V^\nu] \quad ,$$

as long as the external potential does not vanish.

- Finally, time reversal symmetry leads to a twofold degeneracy for purely electrostatic potentials $V^\mu = (V^0, \mathbf{0})$. In this special situation not only the total charge is conserved, but time reversal introduces an additional conserved quantum number.

As a consequence one finds that in the general case, in which $V^\mu(\mathbf{x})$ does not exhibit some specific spatial symmetry and/or some of its components vanish, only the charge and the total energy of the system are conserved. Thus the ground state corresponding to (2.20) is nondegenerate in general. In view of this fact there seems to be no need to introduce a coupling of the electrons (fermions) to an additional external magnetic field \mathbf{B} [19],

$$\hat{H}_{mag} = \frac{e}{4m} \int d^3x \hat{\psi}(x) \sigma_{ij} \hat{\psi}(x) F_{ext}^{ij}(\mathbf{x}) = -\frac{e}{2m} \int d^3x \hat{\psi}(x) \Sigma^k \hat{\psi}(x) B^k(\mathbf{x}) ,$$

in order to lift possible degeneracies as long as the initial vector potential \mathbf{V} is nonzero. Moreover, the interaction of the magnetisation density

$$\hat{m}^k(x) = -\frac{e}{2m} \hat{\psi}(x) \Sigma^k \hat{\psi}(x)$$

with \mathbf{B} does not constitute a fully consistent contribution to the QED-Hamiltonian, as it does not take into account the intrinsic coupling of spin and orbital angular momentum. Thus, while \hat{H}_{mag} may be quite useful under certain physical circumstances (e.g. for weakly relativistic problems), it does not seem to be appropriate as a basis for a RDFT even in the case $V^\mu = (V^0, \mathbf{0})$ [19, 30], in which one might want to split up the degeneracy originating from time reversal symmetry.

As a prerequisite for the discussion of the many body problem implied by the Lagrangian (2.1) a second point needs to be addressed: The theory based on (2.1) is not well defined but rather requires renormalisation of the resulting Greens functions as well as the expressions for physical observables as ground state energies and currents (see Appendix A. for further details). In the present context the renormalisation procedure consists of two steps. The first is the removal of the divergent vacuum (zero point) energy of noninteracting fermions and photons. This is most easily achieved by explicit subtraction of the vacuum expectation value of the Hamiltonian. For instance, if one considers noninteracting electrons not subject to any external potential, i.e. the noninteracting homogeneous electron gas characterised by \hat{H}_e , Eq.(2.21), the renormalised Hamiltonian

$$\hat{H}_R = \hat{H}_e - \langle 0 | \hat{H}_e | 0 \rangle \quad (2.27)$$

leads to a finite ground state energy. The same procedure can be applied to noninteracting photons.

The second part of the renormalisation program, addressing the removal of the ultraviolet (UV) divergencies of QED, which result from the perturbative treatment of the interaction of the fermions with photons and the external field, is more involved. It is instructive to first consider noninteracting fermions in a given external potential,

$$\hat{H}_R = \hat{H}_e + \hat{H}_{ext} - \langle 0 | \hat{H}_e | 0 \rangle \quad , \quad (2.28)$$

where $|0\rangle$ represents the homogeneous vacuum as in (2.27), so that the energy calculated from \hat{H}_R with respect to the perturbed vacuum (often called Casimir energy [31]) is nonzero. While the Greens functions of this theory like the fermion propagator (for a precise definition of the Greens functions see Appendices A.,B.),

$$\begin{aligned} iG(x, y) = & \Theta(x^0 - y^0) \sum_{\epsilon_n > \epsilon_F} \varphi_n(\mathbf{x}) \bar{\varphi}_n(\mathbf{y}) \exp[-i\epsilon_n(x^0 - y^0)] \quad (2.29) \\ & - \Theta(y^0 - x^0) \sum_{\epsilon_F \geq \epsilon_n} \varphi_n(\mathbf{x}) \bar{\varphi}_n(\mathbf{y}) \exp[-i\epsilon_n(x^0 - y^0)] \quad , \end{aligned}$$

where the $\varphi_n(\mathbf{x})$ represent the single particle solutions of the corresponding Dirac equation,

$$\gamma^0 \left\{ -i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m + e\psi(\mathbf{x}) \right\} \varphi_n(\mathbf{x}) = \epsilon_n \varphi_n(\mathbf{x}) , \quad (2.30)$$

are finite without additional modification, the ground state energy and the ground state four current resulting from (2.28) are not [32, 33]. This is most easily seen by rewriting these quantities in terms of $G(x, y)$. Taking the expectation value with respect to the N -electron ground state of the noninteracting system, $|\Phi_0\rangle$, one finds

$$E_{tot} = \langle \Phi_0 | \hat{H}_e + \hat{H}_{ext} | \Phi_0 \rangle - \langle 0 | \hat{H}_e | 0 \rangle \quad (2.31)$$

$$= -i \int d^3x \lim_{y \rightarrow x} \text{tr} \left[\left(-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m + e\psi(\mathbf{x}) \right) G(x, y) \right] \quad (2.32)$$

$$+ i \int d^3x \lim_{y \rightarrow x} \text{tr} \left[\left(-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m \right) G_V^0(x, y) \right]$$

$$j^\nu(\mathbf{x}) = \langle \Phi_0 | \hat{j}^\nu(x) | \Phi_0 \rangle \quad (2.33)$$

$$= -i \lim_{y \rightarrow x} \text{tr} \left[G(x, y) \gamma^\nu \right] , \quad (2.34)$$

where the symmetric limit,

$$\lim_{y \rightarrow x} \equiv \frac{1}{2} \left(\lim_{y \rightarrow x, y^0 > x^0} + \lim_{y \rightarrow x, y^0 < x^0} \right) \Bigg|_{(x-y)^2 \geq 0} , \quad (2.35)$$

is a consequence of the charge conjugation invariant forms (2.21,2.6) and $G_V^0(x, y)$ represents the noninteracting vacuum fermion propagator (A.8). If one now utilises a perturbative expansion of $G(x, y)$ in powers of the external potential,

$$G = \begin{array}{c} \parallel \\ \uparrow \\ \parallel \end{array} + \begin{array}{c} \parallel \\ \bullet \\ \parallel \end{array} \text{---} \text{wavy} \text{---} \times + \begin{array}{c} \parallel \\ \bullet \\ \parallel \\ \bullet \\ \parallel \end{array} \text{---} \text{wavy} \text{---} \times + \dots , \quad (2.36)$$

(for a definition of the diagrammatic representation see Appendices A.-C.) one realises that the evaluation of (2.32,2.34) involves one further loop-integration induced by the symmetric limit, e.g.

$$-i j^\mu = \begin{array}{c} \circlearrowleft \\ \bullet \end{array} + \begin{array}{c} \circlearrowleft \\ \bullet \end{array} \text{---} \text{wavy} \text{---} \times + \begin{array}{c} \circlearrowleft \\ \bullet \end{array} \text{---} \text{wavy} \text{---} \times + \dots . \quad (2.37)$$

Thus the outermost loop integration, by which the quantities E_{tot} and $j^\nu(\mathbf{x})$ (which are of obvious interest in DFT) differ from the UV-finite Greens function G , introduces an UV-divergence completely analogous to the divergencies which arise in standard QED without external fields from the interaction of fermions and photons: Within a perturbative treatment it does not matter whether the external potential $V^\nu(\mathbf{x})$ or the quantised photon field creates virtual electron-positron pairs. As a consequence the renormalisation procedure for E_{tot} and $j^\nu(\mathbf{x})$ is completely determined by the renormalisation of the Greens functions of interacting vacuum QED without external potential. In particular, as discussed in detail in Appendices A.-C. only the second of the diagrams in (2.37) is UV-divergent. The corresponding counterterm $\Delta j^{(0),\nu}(\mathbf{x})$ (the superscript (0) indicates that $\Delta j^{(0),\nu}$ represents the lowest order of the complete counterterm Δj^ν with respect to the electron-electron coupling constant e^2) is explicitly given in Eq.(C.5). The same procedure has to be applied to the ground state energy leading to the counterterm $\Delta E_{tot}^{(0),inhom}$, Eq.(C.10). One thus has to define the renormalised E_{tot} and $j^\nu(\mathbf{x})$ by

$$E_{tot} = \langle \Phi_0 | \hat{H}_e + \hat{H}_{ext} | \Phi_0 \rangle - \langle 0 | \hat{H}_e | 0 \rangle + \Delta E_{tot}^{(0),inhom} \quad (2.38)$$

$$j^\nu(\mathbf{x}) = \langle \Phi_0 | \hat{j}^\nu(\mathbf{x}) | \Phi_0 \rangle + \Delta j^{(0),\nu}(\mathbf{x}) \quad , \quad (2.39)$$

rather than via the initial relations (2.31,2.33).

Finally both the external potential and the quantised photon field have to be considered together, i.e. we have to deal with the full Hamiltonian (2.20). In this case various approaches to the renormalisation procedure are possible. One could e.g. first utilise the standard renormalisation scheme for Greens functions (as summarised in Appendices A.-C.) to generate finite Greens and n -point functions. Expressing the interacting four current $j^\nu(\mathbf{x})$ then in terms of renormalised n -point functions as discussed in Appendix C. one ends up with a finite $j^\nu(\mathbf{x})$. However, there still remains the basic problem of obtaining finite total energies as illustrated above: It is not possible to represent E_{tot} in terms of renormalised Greens functions in such a way that no further (outermost) loop integration is required. This outermost loop integration leads to additional UV-divergencies. Thus in the case of E_{tot} one is forced to renormalise each diagrammatic contribution to the perturbation expansion separately, following the standard rules for the renormalisation of vacuum (sub)graphs (often overlapping divergencies are involved). This procedure is explicitly demonstrated for the case of the exchange-correlation energy of the RHEG in Appendix B.. Quite generally E_{tot} and $j^\nu(\mathbf{x})$ are then given by

$$E_{tot} = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle - \langle 0 | \hat{H}_e + \hat{H}_\gamma + \hat{H}_{int} | 0 \rangle + \Delta E_{tot} \quad (2.40)$$

$$j^\nu(\mathbf{x}) = \langle \Phi_0 | \hat{j}^\nu(\mathbf{x}) | \Phi_0 \rangle + \Delta j^\nu(\mathbf{x}) \quad , \quad (2.41)$$

where the subtraction of the vacuum energy accounts for the fact that in the interacting case all energies can only be measured with respect to the

energy of the interacting, homogeneous vacuum $|0\rangle$. It is sometimes advantageous to decompose the total counterterm ΔE_{tot} into an electron gas part ΔE_{tot}^{RHEG} , which is independent of the external potential, and an inhomogeneity correction,

$$\Delta E_{tot} = \Delta E_{tot}^{RHEG} + \Delta E_{tot}^{inhom} , \quad (2.42)$$

where ΔE_{tot}^{inhom} also involves the full perturbation series with respect to the electron-electron interaction. Eqs.(2.40,2.41) form a suitable starting point for RDFT, as one is now dealing with finite quantities only.

The preceding discussion has been completely based on the Heisenberg representation. The foundations of DFT, on the other hand, are usually formulated within the framework of the Schrödinger picture, so that one might ask in how far this field theoretical procedure can be useful. It is, however, possible to go over to an appropriately chosen Schrödinger representation as long as one does not try to eliminate the quantised photon fields (compare Sections 7d,10g of Ref.[34]). The Hamiltonian then reads

$$\begin{aligned} \hat{H}_S = & \frac{1}{2} \int d^3x \left\{ \left[\hat{\psi}(\mathbf{x}), \left(-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m + e\hat{A}(\mathbf{x}) + e\mathcal{V}(\mathbf{x}) \right) \hat{\psi}(\mathbf{x}) \right] \right. \\ & \left. - \frac{1}{4\pi} \left(\hat{H}_\nu(\mathbf{x}) \hat{H}^\nu(\mathbf{x}) + \boldsymbol{\nabla} \hat{A}_\nu(\mathbf{x}) \cdot \boldsymbol{\nabla} \hat{A}^\nu(\mathbf{x}) \right) \right\} , \end{aligned} \quad (2.43)$$

where the field operators $\hat{\psi}(\mathbf{x})$ and $\hat{A}^\nu(\mathbf{x})$ are now in Schrödinger representation and

$$\hat{H}^\nu(\mathbf{x}) = \exp(-i\hat{H}x^0) \partial_0 \hat{A}_H^\nu(x) \exp(i\hat{H}x^0) .$$

Moreover, all corresponding counterterms (being expectation values) are independent of the representation, so that the renormalisation scheme remains unchanged and it is just a matter of convenience which representation is used. While the Heisenberg representation (2.20) is more suitable for the derivation of explicit functionals, the Hamiltonian (2.43) (together with Eq.(2.40)) can be utilised for the proof of a relativistic Hohenberg-Kohn theorem.

3. Foundations

In this Section we discuss the formal basis of relativistic DFT, that is the relativistic HK-theorem [17, 22], the resulting RKS-equations [18, 19] as well as the relativistic OPM (ROPM) [35, 36]. The discussion of the HK-theorem (in Section 3.1) is restricted to bare essentials, as details have been given in Ref.[22]. In the discussion of the RKS-equations (in Section 3.2) we attempt to outline the transition from the complete equations, including all radiative effects, to practical variants involving various stages of approximations. In Section 3.3 we introduce the ROPM as an extension of the RKS-approach, which, in addition to the kinetic energy also treats the exchange energy within

an orbital scheme⁵. The Section is concluded (Section 3.4) by consideration of the weakly relativistic limit, which allows a connection with and comments on the problem of (nonrelativistic) current density functional theory [37, 38], a topic that involves a number of conceptual questions if one approaches it from the point of view of nonrelativistic theory including magnetic fields.

3.1 Relativistic Hohenberg-Kohn Theorem

The extension of the HK-theorem to relativistic systems was first formulated by Ragagopal and Callaway [17] (see also MacDonald and Vosko [19]). The arguments of these authors are based on QED, but the question of possible UV divergencies was not addressed. As, however, the proof of the theorem on the basis of the celebrated *reductio ad absurdum* involves the comparison of energy values, one has to make sure that proper finite quantities for both the ground state energy as well as the ground state four current are used, i.e. the relativistic HK-theorem must be based on the renormalised quantities (2.40,2.41). In particular, one has to make sure that the structure of the counterterms involved does not invalidate the proof. Here we shall not go through the *reductio ad absurdum* in full detail (for which the interested reader is referred to [22]), but rather summarise the essentials:

- In the first step one shows that there exists a unique map between the set of four potentials $V^\mu(\mathbf{x})$ (up to a global constant in V^0) and the set of ground states $|\Phi_0\rangle$ generated from these potentials. This part of the proof is based on the Hamiltonian (2.43). As only the lack of collinearity of ground states resulting from different external potentials is used at this point (but no energy values are compared) full renormalisation is not required, but rather a suitable regularisation is sufficient (one could e.g. modify the space-time dimension).
- In the second step one analyses the relation between the potential $V^\mu(\mathbf{x})$ and the resulting renormalised ground state four current $j^\mu(\mathbf{x})$, Eq.(2.41). As $j^\mu(\mathbf{x})$ is gauge invariant no one-to-one correspondence between the four current and $V^\mu(\mathbf{x})$ can exist: A unique map can only be established between classes of four potentials $V^\mu(\mathbf{x})$ differing by no more than a static gauge transformation (2.10-2.12) and $j^\mu(\mathbf{x})$. Moreover, the heart of this part of the proof is an inequality between ground state energies, so that the renormalised energies (2.40) must be used. The crucial observation in this context is the fact that the counterterms in (2.40) and (2.41) are completely determined by the external potential: Within a perturbation expansion with respect to $V^\mu(\mathbf{x})$ this is explicitly obvious from Eqs.(2.42,C.9), as the homogeneous counterterm ΔE_{tot}^{RHEG} is identical for all $V^\mu(\mathbf{x})$ and the inhomogeneity correction ΔE_{tot}^{inhom} can be written as a (gauge invariant) functional of $V^\mu(\mathbf{x})$.

⁵ Extension of the OPM to parts of the correlation energy are possible, but far from being standard.

- For the inequality between ground state energies, required for the second step, a minimum principle for the ground state energy (2.40) is used. However, while the Ritz variational principle is well established in the non-relativistic context, we are not aware of any rigorous minimum principle for the renormalised ground state energies resulting from (2.1). There are nevertheless a number of arguments which can be given in favour of such a minimum principle. First of all, with increasing speed of light, i.e. in the nonrelativistic limit ($v/c \rightarrow 0$), the energies (2.40) continuously approach values which do satisfy the Ritz principle. There seems to be no reason to assume the minimum principle to be restricted to the isolated value $c = \infty$. Secondly, one can explicitly verify the minimum principle for a noninteracting inhomogeneous system characterised by the Hamiltonian (2.28), i.e. for the renormalised energies (2.38) within the Furry picture (compare [32, 34]). Finally, real atoms and molecules are stable (indicating that there exists a lower bound for energies) and QED has proven to be the most accurate theory available to date to describe these systems [39] (note further that, as a matter of principle, one need not rely on perturbation theory to deal with QED-systems so that the asymptotic character of this expansion does not contradict this argument).

In summary, one finds that there exists a one-to-one correspondence between the class of external potentials just differing by gauge transformations, the associated class of ground states and the ground state four current,

$$\left\{ V_\nu \mid V_\nu + \partial_\nu \Lambda \right\} \iff \left\{ |\Phi_0 \rangle \mid \text{with } |\Phi_0 \rangle \text{ from } V_\nu + \partial_\nu \Lambda \right\} \iff j^\nu(\mathbf{x}) \quad , \quad (3.1)$$

i.e. the class of physically equivalent ground states is uniquely determined by the ground state four current. Choosing some arbitrary representative of this class, i.e. fixing the gauge once and for all, one can understand this representative $|\Phi_0 \rangle$ as a functional of j^ν , $|\Phi_0[j^\nu] \rangle$, and finally ends up with the statement that all ground state observables are unique functionals of the four current,

$$O[j^\nu] = \langle \Phi_0[j^\nu] \mid \hat{O} \mid \Phi_0[j^\nu] \rangle + \Delta O \quad . \quad (3.2)$$

Of course, the functional $O[j^\nu]$ has to reflect an eventual gauge dependence of the operator \hat{O} and may require renormalisation, indicated by the addition of a counterterm ΔO . Note that, by virtue of the unique correspondence between j^ν and V^ν also all counterterms become functionals of j^ν . For instance, the ground state energy itself, including all counterterms, would be

$$\begin{aligned} E_{tot}[j^\nu] &= \langle \Phi_0[j^\nu] \mid \hat{H} \mid \Phi_0[j^\nu] \rangle - \langle 0 \mid \hat{H}_e + \hat{H}_\gamma + \hat{H}_{int} \mid 0 \rangle \\ &\quad + \Delta E_{tot}^{RHEG} + \Delta E_{tot}^{inhom} \quad . \end{aligned} \quad (3.3)$$

This energy functional contains not only all relativistic kinetic effects for both electrons and photons but also all radiative (that is field-theoretical) effects.

With the Ritz principle and avoiding the question of interacting v -representability, one may then formulate the basic variational principle of RDFT as

$$\frac{\delta}{\delta j^\nu(\mathbf{r})} \left\{ E_{tot}[j^\nu] - \mu \int d^3x j^0(\mathbf{x}) \right\} = 0 . \quad (3.4)$$

The subsidiary condition implies charge conservation and all quantities involved are supposed to be fully renormalised.

For the case of a purely electrostatic external potential, $V^\nu = (V^0, \mathbf{0})$, the complete proof of the relativistic HK-theorem can be repeated using just the zeroth component $j^0(\mathbf{x})$ of the four current (in the following often denoted by the more familiar $n(\mathbf{x})$), i.e. the structure of the external potential determines the minimum set of basic variables for a DFT approach. As a consequence the ground state and all observables, in this case, can be understood as unique functionals of the density n only. This does, however, not imply that the spatial components of the current vanish, but rather that $\mathbf{j}(\mathbf{x}) = \langle \Phi_0[n] | \hat{\mathbf{j}}(\mathbf{x}) | \Phi_0[n] \rangle$ has to be interpreted as a functional of $n(\mathbf{x})$. Thus for standard electronic structure problems one can choose between a four current DFT description and a formulation solely in terms of $n(\mathbf{x})$, although one might expect the former approach to be more useful in applications to systems with $\mathbf{j}(\mathbf{x}) \neq \mathbf{0}$ as soon as approximations are involved. This situation is similar to the nonrelativistic case where for a spin-polarised system not subject to an external magnetic field \mathbf{B} both the $\mathbf{B} \rightarrow \mathbf{0}$ limit of spin-density functional theory as well as the original pure density functional theory can be used. While the former leads in practice to more accurate results for actual spin-polarised systems (as one additional symmetry of the system is taken into account explicitly), both approaches coincide for unpolarised systems.

In view of the two degrees of freedom resulting from time reversal symmetry, one might also set up a two-component formulation of the corresponding RDFT in the special case $V^\nu = (V^0, \mathbf{0})$, which would possibly allow a direct extension of the nonrelativistic spin-density functional formalism. Such an approach has not been investigated on the fully relativistic level. One may, however, interpret the suggestion to use the magnetisation density together with the charge density [19, 30] (and thus the spin-polarised relativistic homogeneous electron gas [30, 40, 41, 42]) as a basis for RDFT as an approximate realisation of such an approach (see also [43, 44]). In the following we shall not address this issue further.

We also mention that recently a density functional approach to excited states of relativistic systems has been formulated [45], using ensembles of unequally weighted states. This formalism is restricted to the electrostatic limit and the no-sea approximation (see Section 3.2). Moreover, it remains unclear how the spontaneous emission of photons, which is possible in QED in contrast to the standard nonrelativistic many-body theory, is handled for the excited states involved.

3.2 Relativistic Kohn-Sham Equations

The basic variational principle (3.4) is applied directly in relativistic (extended) Thomas–Fermi models [12, 21, 46] in which an approximate density functional representation for the complete $E_{tot}[j^\nu]$ is utilised. The mainstay of applications is, however, the KS-scheme. In order to set up this scheme one first introduces auxiliary single particle four spinors $\varphi_k(\mathbf{x})$, in terms of which the exact interacting ground state four current (2.41) is represented as⁶

$$j^\nu(\mathbf{x}) = j_V^\nu(\mathbf{x}) + j_D^\nu(\mathbf{x}) \quad (3.5)$$

$$j_V^\nu(\mathbf{x}) = \frac{1}{2} \left\{ \sum_{\epsilon_k \leq -m} \bar{\varphi}_k(\mathbf{x}) \gamma^\nu \varphi_k(\mathbf{x}) - \sum_{-m < \epsilon_k} \bar{\varphi}_k(\mathbf{x}) \gamma^\nu \varphi_k(\mathbf{x}) \right\} \quad (3.6)$$

$$+ \Delta j^{\nu,(0)}(\mathbf{x})$$

$$j_D^\nu(\mathbf{x}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \bar{\varphi}_k(\mathbf{x}) \gamma^\nu \varphi_k(\mathbf{x}), \quad (3.7)$$

where the counterterm⁷ $\Delta j^{\nu,(0)}(\mathbf{x})$ is given by Eq.(C.5) (with the total RKS-potential on the right hand side) and ϵ_F represents the Fermi level below which all orbitals φ_k are occupied. From a field theoretical point of view the single particle RKS-approach corresponds to a problem of the type (2.28). The form (3.5-3.7) thus follows from the charge conjugation invariant current operator (2.6) via (2.39): The matrix element of j^ν with respect to a noninteracting ground state yields in the first step

$$j^\nu(\mathbf{x}) = \frac{1}{2} \left\{ \sum_{\epsilon_k \leq \epsilon_F} \bar{\varphi}_k(\mathbf{x}) \gamma^\nu \varphi_k(\mathbf{x}) - \sum_{\epsilon_F < \epsilon_k} \bar{\varphi}_k(\mathbf{x}) \gamma^\nu \varphi_k(\mathbf{x}) \right\} + \Delta j^{\nu,(0)}(\mathbf{x}).$$

Rearrangement then gives Eqs.(3.5-3.7) in which the vacuum part $j_V^\nu(\mathbf{x})$ has been separated from the four current $j_D^\nu(\mathbf{x})$ which involves only the discrete occupied orbitals with eigenvalues between $-m$ and ϵ_F .

In the next step one decomposes the ground state energy functional (3.3) in the standard fashion,

$$E_{tot}[j^\nu] = T_s[j^\nu] + E_{ext}[j^\nu] + E_H[j^\nu] + E_{xc}[j^\nu], \quad (3.8)$$

where the counterterms for E_{tot} given in Eq.(2.40) are understood to be included in the individual energy components. The latter are defined as follows: The noninteracting kinetic energy functional T_s , i.e. the kinetic energy of the 'KS-particles', is

⁶ The question of noninteracting v -representability which is required for this representation has not been examined in the relativistic case. One would, however, expect analogous statements as in the nonrelativistic situation [47].

⁷ This term has erroneously been omitted in Ref.[22].

$$T_s[j^\nu] = T_{s,V}[j^\nu] + T_{s,D}[j^\nu] \quad (3.9)$$

$$T_{s,V}[j^\nu] = \frac{1}{2} \int d^3x \left\{ \sum_{\epsilon_k \leq -m} \bar{\varphi}_k(\mathbf{x}) \left[-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m \right] \varphi_k(\mathbf{x}) \right. \quad (3.10)$$

$$\left. - \sum_{-m < \epsilon_k} \bar{\varphi}_k(\mathbf{x}) \left[-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m \right] \varphi_k(\mathbf{x}) \right\}$$

$$T_{s,D}[j^\nu] = \int d^3x \sum_{-m < \epsilon_k \leq \epsilon_F} \bar{\varphi}_k(\mathbf{x}) \left[-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m \right] \varphi_k(\mathbf{x}) , \quad (3.11)$$

where (2.38,C.10,C.13) have to be used to obtain the counterterm ΔT_s^{inhom} . The external potential term is

$$E_{ext} = e \int d^3x j_\mu(\mathbf{x}) V^\mu(\mathbf{x}) , \quad (3.12)$$

(the counterterm (C.12) has already been absorbed into the renormalised current j_μ) and the covariant Hartree energy reads

$$E_H[j^\nu] = \frac{1}{2} \int d^3x \int d^4y j^\mu(\mathbf{x}) D_{\mu\nu}^0(x-y) j^\nu(\mathbf{y}) \quad (3.13)$$

$$= \frac{e^2}{2} \int d^3x \int d^3y \frac{j^\nu(\mathbf{x}) j_\nu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} ,$$

with $D_{\mu\nu}^0$ being the free photon propagator (A.9). The xc-energy functional is then the remainder

$$E_{xc}[j^\nu] = E_{tot}[j^\nu] - T_s[j^\nu] - E_{ext}[j^\nu] - E_H[j^\nu] . \quad (3.14)$$

Note that the ground state energy pertains to the many electron sector. Free photons and positrons are not present in the ground state considered.

One may then use the basic variational principle, varying with respect to the orbitals (a more careful argument can be given following the lines of Ref.[47]), to obtain the complete relativistic KS-equations

$$\gamma^0 \left\{ -i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m + e\psi(\mathbf{x}) + \psi_H(\mathbf{x}) + \psi_{xc}(\mathbf{x}) \right\} \varphi_k(\mathbf{x}) = \epsilon_k \varphi_k(\mathbf{x}) , \quad (3.15)$$

where

$$v_H^\nu(\mathbf{x}) = e^2 \int d^3y \frac{j^\nu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \quad (3.16)$$

$$v_{xc}^\nu(\mathbf{x}) = \frac{\delta E_{xc}[j^\mu]}{\delta j_\nu(\mathbf{x})} . \quad (3.17)$$

Eqs.(3.5,3.15-3.17) have to be solved selfconsistently in order to obtain the exact $j^\nu(\mathbf{x})$ of the interacting system. The corresponding ground state energy is given by

$$\begin{aligned}
E_{tot} &= \frac{1}{2} \left\{ \sum_{\epsilon_k \leq -m} \epsilon_k - \sum_{-m < \epsilon_k} \epsilon_k \right\} - \langle 0 | \hat{H}_e | 0 \rangle + \Delta T_s^{inhom} \\
&+ \sum_{-m < \epsilon_k \leq \epsilon_F} \epsilon_k - E_H[j^\nu] + E_{xc}[j^\nu] - \int d^3x v_{xc}^\nu(\mathbf{x}) j^\nu(\mathbf{x}) \quad .
\end{aligned}$$

The first three terms represent the Casimir energy [31], that is the energy shift induced in the vacuum by the presence of the RKS-potential. In addition, the terms of the second line contain vacuum corrections via both the form (3.5) of j^ν and the functional dependence of E_H , E_{xc} and v_{xc}^μ on j^ν .

A brief glance at the various terms involved in the RKS-scheme reveals a selfconsistency problem of considerable complexity: The evaluation of both j_V^ν and $T_{s,V}$ requires summation over all negative and positive energy solutions and appropriate renormalisation in each step of the iterative procedure. Moreover, all potentials exhibit a four component structure. As the solution of this selfconsistency problem is at best tedious (if at all possible), one is bound to consider a suitable hierarchy of (hopefully) useful approximations.

The most important, and at the same time most legitimate, simplification if one aims at electronic structure calculations in quantum chemistry and condensed matter physics is the *no-sea* (or alternatively *no-pair*) *approximation*. In this approximation all radiative contributions to the four current and T_s are neglected,

$$j_V^\nu(\mathbf{x}) = 0 \quad ; \quad T_{s,V} = 0 \quad . \quad (3.18)$$

In addition the vacuum contributions in the functional dependence of E_{xc} on j^ν are dropped⁸, so that one is led to the RDFT analogue of the no-pair approximation applied in conventional relativistic many-body approaches (see e.g.[7]). An *a posteriori* perturbative evaluation of these corrections is possible and should be adequate, except in special circumstances as for instance the calculation of the structure of super-heavy atoms (with $Z \approx 137$ [33]). The resulting RKS-equations are then still given by Eqs.(3.15-3.17), but $j^\mu(\mathbf{x})$ and T_s are determined by the simpler expressions (3.7) and (3.11).

In addition to the no-sea approximation, two further simplifications may be considered. If the external potential is purely electrostatic

$$\mathbf{V} = \mathbf{0} \quad ; \quad eV^0(\mathbf{r}) = v_{ext}(\mathbf{r}) \quad , \quad (3.19)$$

which is the situation encountered for standard electronic structure calculations, the density $n(\mathbf{r}) = j^0(\mathbf{r})$ is the only quantity which is really required for

⁸ The definition of the no-sea approximation for E_{xc} is not completely unambiguous. As discussed in Appendix B, we define it through neglect of all vacuum fermion loops in the derivation of an approximate $E_{xc}[j^\nu]$. Alternatively, one could project out all negative energy states, thus generating a direct equivalent of the standard no-pair approximation. As one would expect the differences between these two schemes to be small, we do not differentiate between these approximations here.

the RDFT scheme (as discussed in the previous Section). In this *electrostatic limit* the spatial current \mathbf{j} and also the energy components (3.9-3.14) can be understood as functionals of n only and RDFT reduces to a pure density functional approach. The structure of the density functional representations for E_H and E_{xc} is determined by the original functionals $E_H[j^\nu]$ and $E_{xc}[j^\nu]$ by simply inserting the exact density functional for \mathbf{j} ,

$$\tilde{E}_H[n] = E_H[n, \mathbf{j}[n]] \quad , \quad \tilde{E}_{xc}[n] = E_{xc}[n, \mathbf{j}[n]] \quad . \quad (3.20)$$

The corresponding RKS-equations are then given by (3.15) with the Hartree and xc-potentials consisting only of a time-like component $\tilde{v}_{H,xc}(\mathbf{r})$,

$$\tilde{v}_{H,xc}(\mathbf{r}) = \frac{\delta \tilde{E}_{H,xc}[n]}{\delta n(\mathbf{r})} = \frac{\delta E_{H,xc}[j^\nu]}{\delta n(\mathbf{r})} + \int d^3 r' \frac{\delta E_{H,xc}[j^\nu]}{\delta j^k(\mathbf{r}')} \frac{\delta j^k([n], \mathbf{r}')}{\delta n(\mathbf{r})} \quad ,$$

so that their structure is considerably simplified.

An additional approximation can be obtained if one uses the decomposition of the electron-electron interaction mediated by the free photon propagator $D_{\mu\nu}^0$ into a longitudinal and a transverse part (according to Eq.(A.10)) to introduce the corresponding decomposition for E_H and E_{xc} ,

$$E_H[n] = E_H^L[n] + E_H^T[n] \quad ; \quad E_{xc}[n] = E_{xc}^L[n] + E_{xc}^T[n] \quad (3.21)$$

(in the following we shall only distinguish between the functionals in the electrostatic limit, $\tilde{E}_{H,xc}[n] \equiv E_{H,xc}[n]$, and the more general $E_{H,xc}[j^\nu]$ by their respective arguments). While this decomposition is obvious for $E_H[n]$,

$$E_H^L[n] = \frac{e^2}{2} \int d^3 r \int d^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (3.22)$$

$$E_H^T[\mathbf{j}[n]] = -\frac{e^2}{2} \int d^3 r \int d^3 r' \frac{\mathbf{j}([n]; \mathbf{r}) \cdot \mathbf{j}([n]; \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad , \quad (3.23)$$

which is linear in $D_{\mu\nu}^0$, E_{xc}^L is defined by neglecting the transverse interaction to all orders in $D_{\mu\nu}^0$ (and the remainder is then called E_{xc}^T).

The *longitudinal approximation* then consists in neglecting the transverse contributions E_H^T and E_{xc}^T in the selfconsistency loop, i.e.

$$v_H^T(\mathbf{r}) = 0 \quad ; \quad v_{xc}^T(\mathbf{r}) = 0 \quad . \quad (3.24)$$

The transverse contributions to the ground state energy can then be calculated *a posteriori* in a perturbative fashion. As most available energy functionals in RDFT include both longitudinal and transverse contributions and the selfconsistency problem is not simplified by the longitudinal approximation, this approximation is not required for an efficient application of the RKS-equations. Rather it leads to the RDFT-equivalent of the so-called Dirac-Coulomb Hamiltonian usually applied in conventional *ab initio* calculations,

so that it is mainly useful for purposes of comparison⁹. Note that the longitudinal approximation does not automatically imply the neglect of all current contributions to the xc-potential (and vice versa) as one might expect on the basis of $E_H[j^\nu]$, for which these two approximations coincide. This point is most readily demonstrated by the current-dependence of explicit current-density functional representations of T_s (as discussed in Appendix D.).

If one restricts oneself to the electrostatic limit of RDFT and relies on both the no-sea as well as the longitudinal approximation one arrives at the RKS-equations

$$\left\{ -i\boldsymbol{\alpha}\cdot\nabla + \beta m + v_{tot}^L(\mathbf{r}) \right\} \varphi_k(\mathbf{r}) = \epsilon_k \varphi_k(\mathbf{r}), \quad (3.25)$$

where $\boldsymbol{\alpha}, \beta$ are the usual Dirac matrices and

$$v_{tot}^L(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H^L([n]; \mathbf{r}) + v_{xc}^L([n]; \mathbf{r}) \quad (3.26)$$

$$v_H^L([n]; \mathbf{r}) = e^2 \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (3.27)$$

$$v_{xc}^L([n]; \mathbf{r}) = \frac{\delta E_{xc}^L[n]}{\delta n(\mathbf{r})} \quad (3.28)$$

$$n(\mathbf{r}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi_k^\dagger(\mathbf{r}) \varphi_k(\mathbf{r}) . \quad (3.29)$$

Referring to the various approximations suggested, the corresponding ground state energy is obtained as

$$E_{tot}^L = T_{s,D} + E_{ext} + E_H^L + E_{xc}^L , \quad (3.30)$$

which may be corrected by addition of the transverse energy terms,

$$E_{tot} = E_{tot}^L + E_H^T + E_{xc}^T , \quad (3.31)$$

as well as radiative corrections. The scheme (3.25-3.30) corresponds to the no-pair Dirac-Coulomb Hamiltonian of standard relativistic many-body theory. Selfconsistent treatment of the transverse contributions, on the other hand, would lead to the RDFT-version of the no-pair Dirac-Coulomb-Breit Hamiltonian, ignoring the small difference between the full transverse and the Breit interaction.

A time-dependent generalisation of the RKS-equation (3.25) has been suggested by Parpia and Johnson [49]. While a rigorous foundation of this approach is not available to date, this method has been successfully applied to the photoionisation of Hg [50] and Xe [49] as well as the evaluation of the polarisabilities of heavy closed-shell atoms [51] (using a direct time-dependent extension of the local density approximation for $E_{xc}[n]$).

⁹ A selfconsistent treatment of the transverse interaction in conventional *ab initio* methods is often based on the Gaunt approximation [48]. There are, however, no density functionals available within this approximation.

3.3 Optimised-Potential Method

The important observation leading to the transition from the original variational approach (3.4) to the KS-equations is the fact that all currently available density functional representations of the kinetic energy are not able to reproduce one of the most basic features of quantum systems, i.e. the electronic shell structure. Thus, as soon as one is interested in properties of quantum systems which are related to the shell structure (i.e. merely all), one is forced to go to the equivalent KS single particle problem and treat its kinetic energy exactly¹⁰. The next important physical feature for which an accurate density functional representation is currently not at hand is the cancellation of the self interaction effects to be provided by the exchange energy functional. A natural route to circumvent this problem is to resort to an orbital representation for the exchange part of the xc-energy and to treat the resulting extended single particle problem exactly. In the nonrelativistic context this extension of the selfconsistency problem to include exchange on an exact level was originally introduced by Talman and Shadwick [52] (see also [53]) and has later been adopted as a DFT-method by Sahni, Gruenebaum and Perdew [54] as well as Langreth and Mehl [55] and Sham [56] under the name of the optimised-potential-method (OPM). It should be viewed as a systematic extension of the KS-scheme and thus its relativistic extension is also discussed in this Section devoted to the foundations of RDFT. The OPM selfconsistency procedure is much more involved than the KS-scheme and thus applications beyond spherical systems [57, 58, 59, 60] or the atomic sphere approximation in band structure calculations [61, 62] are lacking to date. This approach has, however, attracted considerable attention (see e.g. [63, 64]) since an accurate, approximate solution of the crucial OPM equation for the exchange potential has been given by Krieger, Li and Iafrate [58, 65, 66, 67].

A relativistic extension of the OPM on the longitudinal no-pair level has been put forward by Talman and collaborators [35] (and recently been applied to atoms [36]). Further extension to a covariant exchange energy functional is straightforward on the basis of the RKS propagator G_{KS} ,

$$E_x = \frac{1}{2} \int d^3x \int d^4y D_{\mu\nu}^0(x-y) \text{tr} \left[G_{KS}(x,y) \gamma^\nu G_{KS}(y,x) \gamma^\mu \right] , \quad (3.32)$$

(the required counterterms are not explicitly shown). The propagator G_{KS} describes the motion of the 'KS-particles' in the total RKS-potential. It can be expressed in terms of the RKS-orbitals via the standard expansion (2.29). The exchange energy functional defined in this fashion should not be confused

¹⁰ Note that quite generally the rearrangement of the ground state energy functional by addition and subtraction of terms, that leads to the KS-scheme, is quite arbitrary. Instead of adding and subtracting e.g. the kinetic energy T_s any other suitable approximation of the full kinetic energy could be used, resulting in a modified selfconsistency problem.

with the relativistic HF (RHF) exchange energy (at least from a rigorous point of view), as the RKS-orbitals satisfy the local RKS-equations (3.15) rather than the nonlocal RHF-equations.

The energy (3.32) is, via the (rather involved) dependence of the RKS-orbitals on the four current density, a functional of this quantity,

$$E_x = E_x[j^\nu] . \quad (3.33)$$

The RDFT correlation energy is then defined by

$$E_c[j^\nu] = E_{xc}[j^\nu] - E_x[j^\nu] . \quad (3.34)$$

and the individual potentials are

$$v_x^\mu([j^\nu]; \mathbf{r}) = \frac{\delta E_x[j^\nu]}{\delta j_\mu(\mathbf{r})} \quad (3.35)$$

$$v_c^\mu([j^\nu]; \mathbf{r}) = \frac{\delta E_c[j^\nu]}{\delta j_\mu(\mathbf{r})} . \quad (3.36)$$

If $E_c[j^\nu]$ is neglected the resulting scheme is called the exchange-only (x-only) limit of RDFT.

For the case of the longitudinal no-pair approximation and a purely electrostatic external potential $V^\mu = (V^0, \mathbf{0})$, to which we restrict further discussion of the ROPM, Eq.(3.32) reduces to (summation over the spinor indices $a, b = 1, \dots, 4$ is implicitly understood)

$$E_x^L[n] = -\frac{e^2}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \sum_{-m < \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\varphi_{a,k}^+(\mathbf{r}) \varphi_{b,l}^+(\mathbf{r}') \varphi_{a,l}(\mathbf{r}) \varphi_{b,k}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} , \quad (3.37)$$

where the φ_k now have to be interpreted as functionals of the density only. The crucial feature of $E_x^L[n]$ is its linear dependence on the electron-electron coupling constant e^2 : The functional dependence of the φ_k on n is independent of e^2 as the φ_k experience a local (in the sense of multiplicative) one-body potential [54, 55, 56], where it does not matter whether the local potential is obtained selfconsistently or is just a given external potential. The correlation energy functional $E_c^L[n]$ thus contains all contributions to $E_{xc}^L[n]$ which are of higher order in e^2 .

As the exact density dependence of $\varphi_k([n]; \mathbf{r})$ is not known, however, the corresponding x-only potential $v_x^L(\mathbf{r})$ can not be directly evaluated via (3.35). Nevertheless, utilising the fact that the one-body potential which minimises $E_{tot}^L[n]$ is unique [54, 55, 56], v_x^L can be obtained by minimisation of the total ground state energy with respect to the total one-body potential (3.26) which the φ_k experience,

$$\frac{\delta E_{tot}^L[n]}{\delta v_{tot}^L(\mathbf{r})} = \int d^3r' \sum_{-m < \epsilon_k \leq \epsilon_F} \frac{\delta E_{tot}^L[n]}{\delta \varphi_k(\mathbf{r}')} \frac{\delta \varphi_k(\mathbf{r}')}{\delta v_{tot}^L(\mathbf{r})} + c.c. = 0 . \quad (3.38)$$

Decomposing v_{tot}^L according to (3.26) and

$$v_{xc}^L(\mathbf{r}) = v_x^L(\mathbf{r}) + v_c^L(\mathbf{r}) , \quad (3.39)$$

one obtains an integral equation for $v_x^L(\mathbf{r})$,

$$\int d^3r' K(\mathbf{r}, \mathbf{r}') v_x^L(\mathbf{r}') = Q(\mathbf{r}) . \quad (3.40)$$

The kernel of the integral equation is given by

$$K(\mathbf{r}, \mathbf{r}') = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi_k^+(\mathbf{r}) G_k(\mathbf{r}, \mathbf{r}') \varphi_k(\mathbf{r}') , \quad (3.41)$$

while the inhomogeneous term reads

$$\begin{aligned} Q(\mathbf{r}) = & -e^2 \sum_{-m < \epsilon_k, \epsilon_l \leq \epsilon_F} \int d^3r' \int d^3r'' \\ & \times \varphi_k^+(\mathbf{r}) G_k(\mathbf{r}, \mathbf{r}') \frac{\varphi_l(\mathbf{r}') \varphi_l^+(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \varphi_k(\mathbf{r}'') . \end{aligned} \quad (3.42)$$

The quantity $G_k(\mathbf{r}, \mathbf{r}')$ represents the Greens function

$$G_k(\mathbf{r}, \mathbf{r}') = \sum_{-m < \epsilon_l < m, l \neq k} \frac{\varphi_l(\mathbf{r}) \varphi_l^+(\mathbf{r}')}{\epsilon_l - \epsilon_k} , \quad (3.43)$$

which satisfies

$$\begin{aligned} & \left[-i\boldsymbol{\alpha} \cdot \boldsymbol{\nabla} + \beta m + v_{tot}^L(\mathbf{r}) - \epsilon_k \right] G_k(\mathbf{r}, \mathbf{r}') \\ & = \delta^{(3)}(\mathbf{r} - \mathbf{r}') - \varphi_k(\mathbf{r}) \varphi_k^+(\mathbf{r}') . \end{aligned} \quad (3.44)$$

The longitudinal no-pair ROPM thus requires the simultaneous selfconsistent solution of (3.40)¹¹ and the RKS-equation (3.25), either including some correlation potential or in the x-only limit with $v_c^L = 0$.

The advantage of the ROPM lies in the fact that due to the Fock form of $E_x^L[n]$ the self interaction of the 'KS-particles' is cancelled exactly. This also manifests itself in the asymptotic form of v_x^L for finite systems,

$$v_x^L(r \rightarrow \infty) \rightarrow -\frac{1}{r} , \quad (3.45)$$

so that the total potential is free of self interaction effects, e.g. for neutral systems one obtains

¹¹ The integral equation (3.40) determines v_x^L up to a trivial constant which is determined by the boundary condition $v_x^L(r \rightarrow \infty) = 0$.

$$v_{tot}^L(r \rightarrow \infty) \rightarrow -\frac{1}{r} . \quad (3.46)$$

In order to provide a quantitative comparison of this DF-concept for exchange and the standard HF approach we list in Table 3.1 the corresponding x-only ground state energies and eigenvalues of the highest occupied orbitals for spherical (closed subshell) atoms [36]. As is obvious from Table 3.1 the

Table 3.1. Longitudinal ground state energies ($-E_{tot}^L$) and highest occupied eigenvalues ($-\epsilon_{mk}^L$) for closed subshell atoms from nonrelativistic OPM (NROPM [59]), relativistic OPM (ROPM [36]) and relativistic HF (RHF [68]) calculations [69] (all energies are in hartree).

Atom	$-E_{tot}^L$			$-\epsilon_{mk}^L$		
	NROPM	ROPM	RHF	NROPM	ROPM	RHF
He (1S1/2)	2.862	2.862	2.862	0.918	0.918	0.918
Be (2S1/2)	14.572	14.575	14.576	0.309	0.309	0.309
Ne (2P3/2)	128.545	128.690	128.692	0.851	0.848	0.848
Mg (3S1/2)	199.611	199.932	199.935	0.253	0.253	0.253
Ar (3P3/2)	526.812	528.678	528.684	0.591	0.587	0.588
Ca (4S1/2)	676.751	679.704	679.710	0.196	0.196	0.196
Zn (4S1/2)	1777.828	1794.598	1794.613	0.293	0.299	0.299
Kr (4P3/2)	2752.028	2788.848	2788.861	0.523	0.515	0.514
Sr (5S1/2)	3131.514	3178.067	3178.080	0.179	0.181	0.181
Pd (4D5/2)	4937.858	5044.384	5044.400	0.335	0.319	0.320
Cd (5S1/2)	5465.056	5593.299	5593.319	0.266	0.282	0.281
Xe (5P3/2)	7232.018	7446.876	7446.895	0.456	0.439	0.440
Ba (6S1/2)	7883.404	8135.625	8135.644	0.158	0.163	0.163
Yb (6S1/2)	13391.070	14067.621	14067.669	0.182	0.196	0.197
Hg (6S1/2)	18408.313	19648.826	19648.865	0.262	0.329	0.328
Rn (6P3/2)	21865.826	23601.969	23602.005	0.427	0.382	0.384
Ra (7S1/2)	23093.258	25028.027	25028.061	0.149	0.167	0.166
No (7S1/2)	32787.471	36740.625	36740.682	0.171	0.209	0.209

differences between ROPM and RHF ground state energies are rather small from a numerical point of view: They are below 60 mhartree even for the largest atoms, with the ROPM-energies always being somewhat less attractive (consistent with the reduced variational freedom of the ROPM-orbitals) — apart from He where both approaches coincide. Also the corresponding highest occupied eigenvalues are essentially identical. The same holds for the longitudinal x-only energies (see Table 5.1). Here the maximum difference of 106 mhartree is found for No. The x-only ROPM thus demonstrates explicitly that one can obtain RHF-level results for all interesting atomic properties with a local exchange potential.

3.4 Nonrelativistic Limit

The weakly relativistic limit of the Hamiltonian (2.20) for fermions in external electric and magnetic fields can be derived with standard techniques, either by direct expansion or by a low order Foldy-Wouthuysen transformation. One obtains

$$\hat{H} = \int d^3x \hat{\varphi}^+(\mathbf{x}) \left\{ \frac{1}{2m} [(-i\hbar\nabla)^2 + 2i\hbar\frac{e}{c}\mathbf{V}(\mathbf{x}) \cdot \nabla + \frac{e^2}{c^2}\mathbf{V}(\mathbf{x})^2] - \frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot (\nabla \times \mathbf{V}(\mathbf{x})) + eV_0(\mathbf{x}) \right\} \hat{\varphi}(\mathbf{x}) + \hat{H}_{ee} \quad (3.47)$$

In Eq.(3.47) $\hat{\varphi}(\mathbf{x})$ is a nonrelativistic field operator of two component structure, $\boldsymbol{\sigma}$ are the Pauli matrices and the electron-electron interaction reduces to the Coulomb interaction, denoted by \hat{H}_{ee} . As usual, the gauge term proportional to $(e^2/c^2)\mathbf{V}(\mathbf{x})^2$ has been kept, although it is of order $1/c^2$ and terms of this order are not included consistently. The Hamiltonian (3.47) is invariant under the gauge transformation

$$\hat{\varphi}'(\mathbf{x}) = e^{-ie\lambda(\mathbf{x})/\hbar} \hat{\varphi}(\mathbf{x}) \quad , \quad \mathbf{V}'(\mathbf{x}) = \mathbf{V}(\mathbf{x}) - c\nabla\lambda(\mathbf{x}) \quad , \quad (3.48)$$

i.e.

$$H(\hat{\varphi}', \mathbf{V}') = H(\hat{\varphi}, \mathbf{V}) \quad .$$

The density operator is defined in terms of the field operators as

$$\hat{n}(\mathbf{x}) = \hat{\varphi}^+(\mathbf{x}) \hat{\varphi}(\mathbf{x}) \quad , \quad (3.49)$$

and by a weakly relativistic expansion of the current operator (2.6) (together with the appropriate redefinition of the vacuum) the following expression for the nonrelativistic current operator can be extracted,

$$\hat{\mathbf{j}}(\mathbf{x}) = \hat{\mathbf{j}}_p(\mathbf{x}) - \frac{c}{e} \nabla \times \hat{\mathbf{m}}(\mathbf{x}) - \frac{e}{mc} \mathbf{V}(\mathbf{x}) \hat{n}(\mathbf{x}) \quad . \quad (3.50)$$

Here the paramagnetic current,

$$\hat{\mathbf{j}}_p(\mathbf{x}) = -\frac{i\hbar}{2m} \left[\hat{\varphi}^+(\mathbf{x}) (\nabla \hat{\varphi}(\mathbf{x})) - (\nabla \hat{\varphi}^+(\mathbf{x})) \hat{\varphi}(\mathbf{x}) \right] \quad , \quad (3.51)$$

and the magnetisation-density,

$$\hat{\mathbf{m}}(\mathbf{x}) = -\frac{e\hbar}{2mc} \hat{\varphi}^+(\mathbf{x}) \boldsymbol{\sigma} \hat{\varphi}(\mathbf{x}) \quad , \quad (3.52)$$

are defined as usual. It is important to note that $\hat{\mathbf{j}}_p(\mathbf{x})$ is not invariant under the gauge transformation (3.48), only the combination

$$\hat{\mathbf{j}}_p(\mathbf{x}) - \frac{e}{mc} \mathbf{V}(\mathbf{x}) \hat{n}(\mathbf{x})$$

has this property.

If one reexpresses the Hamiltonian (3.47) in terms of the density and current operators in order to exhibit the coupling to the external fields more explicitly, one finds

$$\begin{aligned} \hat{H} = & \int d^3x \left\{ \hat{\varphi}^+(\mathbf{x}) \frac{(-i\hbar\nabla)^2}{2m} \hat{\varphi}(\mathbf{x}) + eV_0(\mathbf{x})\hat{n}(\mathbf{x}) \right\} + \hat{H}_{ee} \\ & - \int d^3x \frac{e}{c} \mathbf{V}(\mathbf{x}) \cdot \left\{ \hat{\mathbf{j}}_p(\mathbf{x}) - \frac{c}{e} \nabla \times \hat{\mathbf{m}}(\mathbf{x}) - \frac{e}{2mc} \mathbf{V}(\mathbf{x})\hat{n}(\mathbf{x}) \right\}. \end{aligned} \quad (3.53)$$

This expression indicates that it is the sum of the paramagnetic current operator and the curl of the magnetisation density,

$$\hat{\mathbf{j}}_p(\mathbf{x}) - \frac{c}{e} \nabla \times \hat{\mathbf{m}}(\mathbf{x}) ,$$

which couples to the external vector potential, but the situation is somewhat ambiguous concerning the gauge term, as one may rearrange the Hamiltonian (3.53) either in the form

$$\hat{H} = \hat{T} + \hat{H}_{ee} + \int d^3x \left\{ -\frac{e}{c} \mathbf{V}(\mathbf{x}) \cdot \hat{\mathbf{j}}(\mathbf{x}) + \left[eV_0(\mathbf{x}) - \frac{e^2}{2mc^2} \mathbf{V}(\mathbf{x})^2 \right] \hat{n}(\mathbf{x}) \right\} , \quad (3.54)$$

or

$$\begin{aligned} \hat{H} = & \hat{T} + \hat{H}_{ee} - \int d^3x \frac{e}{c} \mathbf{V}(\mathbf{x}) \cdot \left[\hat{\mathbf{j}}_p(\mathbf{x}) - \frac{c}{e} \nabla \times \hat{\mathbf{m}}(\mathbf{x}) \right] \\ & + \int d^3x \left[eV_0(\mathbf{x}) + \frac{e^2}{2mc^2} \mathbf{V}(\mathbf{x})^2 \right] \hat{n}(\mathbf{x}) . \end{aligned} \quad (3.55)$$

It is directly possible to prove a HK-theorem for the form (3.55) using the density n and the gauge dependent current $\mathbf{j}_p - (c/e)\nabla \times \mathbf{m}$ as basic DFT variables, but not for the form (3.54) which would suggest to use n and the full current \mathbf{j} . One is thus led to the statement that the first set of variables can legitimately be used to set up nonrelativistic current density functional theory, indicating at first glance a conflict with the fully relativistic DFT approach.

It is important to notice, however, that consistent neglect of all terms of the order $1/c^2$ (which has not been treated consistently in the weakly relativistic expansion) in the Hamiltonian allows a proof of a HK-theorem on the basis of the variables n and \mathbf{j} . In other words: Only a fully relativistic approach combines consistency in $1/c$ with gauge invariance. It remains to be investigated explicitly, whether inclusion of all relevant terms to order $1/c^2$ allows to reinstate the physical current $\mathbf{j}(\mathbf{x})$ as basic variable also in this order as one would expect from the fully relativistic theory.

4. Explicit Relativistic Exchange-Correlation Functionals

The derivation of explicit energy functionals in *nonrelativistic* DFT follows a variety of avenues. The present day "standard" is the LDA,

$$E_{xc}^{NRLDA}[n] = \int d^3r e_{xc}^{NRHEG}(n(\mathbf{r})), \quad (4.1)$$

in which the density dependence of the xc-energy density e_{xc}^{NRHEG} of the nonrelativistic HEG is used with the density $n(\mathbf{r})$ of the actual inhomogeneous system. In particular, accurate representations of the correlation part e_c^{NRHEG} [70, 71, 72, 73] are obtained by a parametrisation of Monte Carlo results for the NRHEG [74, 73]. Gradient corrections in low order,

$$E_{xc}^{NRGE}[n] = \int d^3r e_{xc}^{NRGE}(n(\mathbf{r}), (\nabla n(\mathbf{r}))^2, \nabla^2 n(\mathbf{r})) \quad (4.2)$$

were first obtained by painstaking analysis of the relevant diagrammatic contributions (see e.g.[75, 76, 77, 78, 79, 80, 81, 60]), but turned out not to be adequate [75, 76, 82]. The situation was improved by the introduction of generalised gradient approximations (GGAs) [10, 11, 83, 84, 85, 86], in which $(\nabla n)^2$ -terms beyond the lowest order contribution to the gradient expansion (GE) are included. These types of functionals yield the most accurate values for atomic ground state and ionisation energies, molecular geometries and dissociation energies as well as cohesive properties of solids that have been obtained to date with nonrelativistic density functionals (see e.g.[2, 3, 82, 87, 88, 89, 90, 91]).

An alternative approach under the heading of weighted density approximation (WDA) attempts to model the density dependence of the pair correlation function of inhomogeneous systems,

$$E_{xc}^{NRWDA}[n] = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} [\tilde{g}([n]; \mathbf{r}, \mathbf{r}') - 1], \quad (4.3)$$

where \tilde{g} indicates that a coupling constant integration over the pair correlation function is involved. The WDA is characterised by the feature that self interaction effects are corrected to a large degree, though not as completely as in the OPM.

Compared with the nonrelativistic case, the derivation of explicit relativistic functionals is not as fully developed. Concerning the RLDA both the x-only limit and the correlation contribution in the so-called random phase approximation (RPA) are available. We discuss the RLDA in Section 4.1. Relativistic gradient corrections for E_{xc} , on the other hand, have not been evaluated at all, although the basic technique for their derivation can be extended to the relativistic regime. In view of the absence of explicit results we only illustrate this method for the case of T_s in Appendix D.. An extension of

the WDA scheme to relativistic systems (RWDA) [92, 36] is summarised in Section 4.2. However, no information on the RWDA beyond the longitudinal x-only limit is available. Moreover, it should be emphasised at the very outset that on the present level of sophistication neither the RLDA nor the RWDA contain radiative corrections. The issue of vacuum corrections in $E_{xc}[n]$ is discussed in detail in Appendix B. and will not be addressed in this Section.

4.1 Relativistic Local Density Approximation

In complete analogy to (4.1) the RLDA for $E_{xc}[j^\nu]$ is based on the xc-energy density $e_{xc}^{RHEG}(n)$ of the relativistic homogeneous electron gas (RHEG), which automatically reduces the full j^ν -dependence of the exact xc-energy functional to a pure density dependence,

$$E_{xc}^{RLDA}[n] = \int d^3r e_{xc}^{RHEG}(n_0 = n(\mathbf{r})) . \quad (4.4)$$

The derivation of its lowest order contribution, i.e. the exchange energy, is discussed in some detail in Appendix B., illustrating in particular the UV-renormalisation required¹². The final result, that has been obtained by a number of authors [93, 94, 95, 96, 18, 19], can be expressed as the nonrelativistic exchange energy density e_x^{NRHEG} multiplied by a relativistic correction factor. Separation into its longitudinal and transverse part according to (3.21) yields,

$$e_x^{RHEG,L/T}(n) = e_x^{NRHEG}(n) \Phi_x^{L/T}(\beta) , \quad (4.5)$$

where β represents the basic relativistic density variable,

$$\beta = \frac{(3\pi^2 n)^{\frac{1}{3}}}{mc} , \quad (4.6)$$

and $e_x^{NRHEG}(n)$ and the $\Phi_x^{L/T}$ are explicitly given in (B.51, B.54, B.55). The variation of the $\Phi_x^{L/T}$ with β is shown in Fig.4.1. One notices that the longitudinal contribution dominates in the low density limit and that it depends only weakly on β . The transverse part shows a stronger dependence on β and dominates in the high density regime, in which e_x^{RHEG} even changes its sign.

The transverse part can be analysed further if one separates it into a magnetic (or current-current) and a retardation component or if one restricts oneself to its weakly relativistic limit, the so-called Breit contribution [48, 97],

$$e_x^{RHEG,T} = e_x^{mag} + e_x^{ret} = e_x^{T,Breit} + \dots ,$$

where the individual terms follow from the structure of the transverse photon propagator $D_{\mu\nu}^{0,T}$,

¹² Note that in the case of e_x^{RHEG} vacuum corrections do not contribute after renormalisation, so that the complete result is identical with its no-sea/pair approximation.

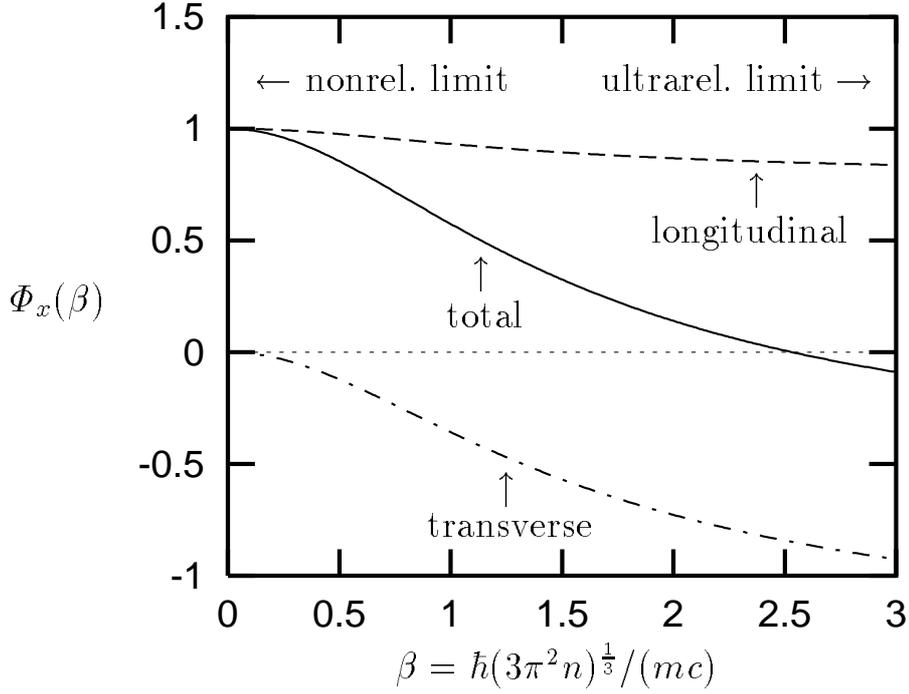


Fig. 4.1. Relativistic correction factor for the LDA exchange energy density: Longitudinal contribution (B.54), transverse contribution (B.55) and total correction $\Phi_x^L + \Phi_x^T$.

$$\begin{aligned}
 D_{00}^{0,T}(k) &= \frac{-4\pi e^2}{k^2 + i\epsilon} - \frac{4\pi e^2}{\mathbf{k}^2} = \frac{4\pi e^2 (k^0)^2}{\mathbf{k}^4} + \dots \\
 &\Rightarrow \text{retardation of charge-charge interaction} \\
 D_{ij}^{0,T}(k) &= \delta_{ij} \frac{4\pi e^2}{k^2 + i\epsilon} = \delta_{ij} \frac{-4\pi e^2}{\mathbf{k}^2} + \dots \\
 &\Rightarrow \text{magnetic interaction (= Gaunt interaction + ...)} \quad ,
 \end{aligned}$$

inserted into (3.32). The density dependence of these terms is illustrated in Fig.4.2, which shows that the behaviour of e_x^T is largely dominated by the magnetic contribution. The relative minor role of higher order retardation effects is emphasised by the similarity between e_x^T and $e_x^{T,Breit}$.

In Fig.4.3 we plot the density dependence of the resulting exchange potentials. The relevant range of density values for electronic structure calculations is indicated by the β -values at the origin and the expectation value of the radial coordinate of the $1S_{1/2}$ -orbital for the Kr and Hg atoms. One finds that relativistic effects are somewhat more pronounced for v_x than for e_x and are definitely relevant for inner shell features of high Z-atoms.

Relativistic correlation contributions in the LDA have so far only been considered on the basis of a partial resummation of those terms in the perturbation expansion in e^2 which are the most relevant in the high density limit. This contribution is either called the ring approximation (in accordance

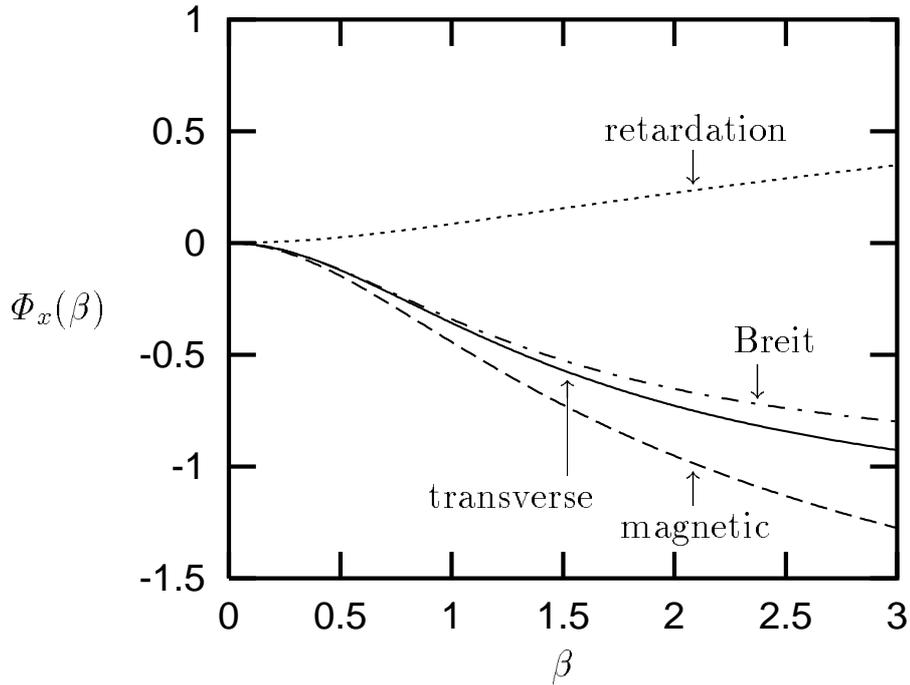


Fig. 4.2. Relativistic correction factor for the LDA exchange energy density: Magnetic, retardation and Breit contribution ($e_x^{T,Breit}$ from Ref.[97] has been corrected for a typographical error).

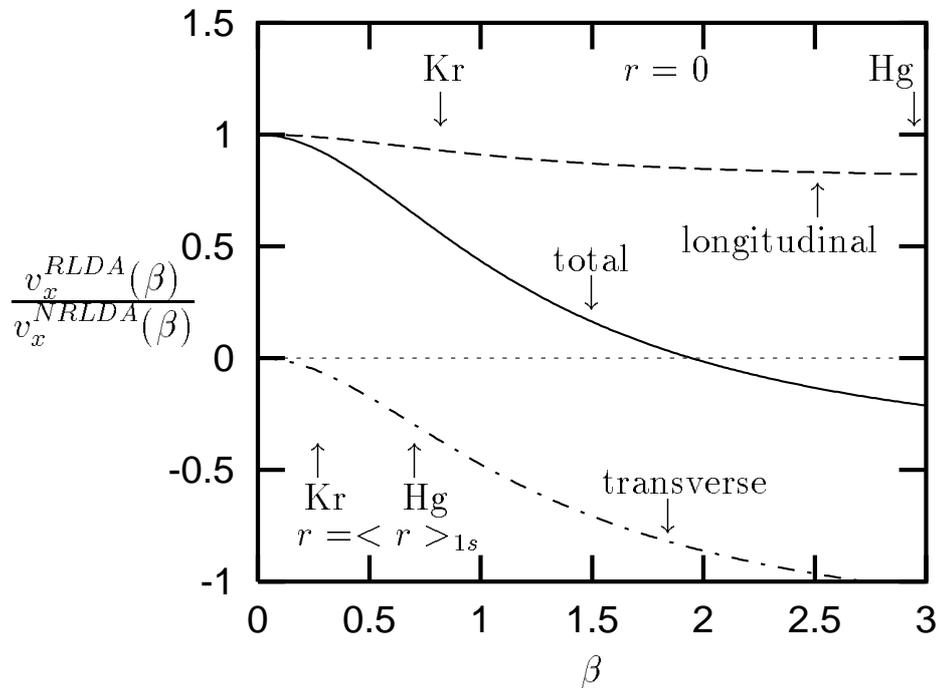


Fig. 4.3. Relativistic correction factor for the LDA exchange potential. The values of the densities of Kr and Hg at the origin ($r = 0$) and the r -expectation values of the $1s$ -orbitals ($r = \langle r \rangle_{1s}$) from RLDA-calculations using finite nuclei are also indicated.

with its diagrammatic form) or, most often, the random phase approximation (RPA — which we shall use here) to e_c^{RHEG} . The detailed discussion of $e_c^{RHEG,RPA}$ is again relegated to Appendix B. In contrast to the case of exchange no closed analytical expression can be given for $e_c^{RHEG,RPA}$. Numerical results (within the no-sea approximation) have been obtained by Ramana and Rajagopal [98] and by Müller and Serot [99]. The resulting relativistic correction factor,

$$e_c^{RHEG,RPA}(n) = e_c^{NRHEG,RPA}(n) \Phi_c^{RPA}(\beta) , \quad (4.7)$$

(again decomposed into its longitudinal and transverse contributions) is shown in Fig.4.4. As for the exchange energy the relativistic correction for

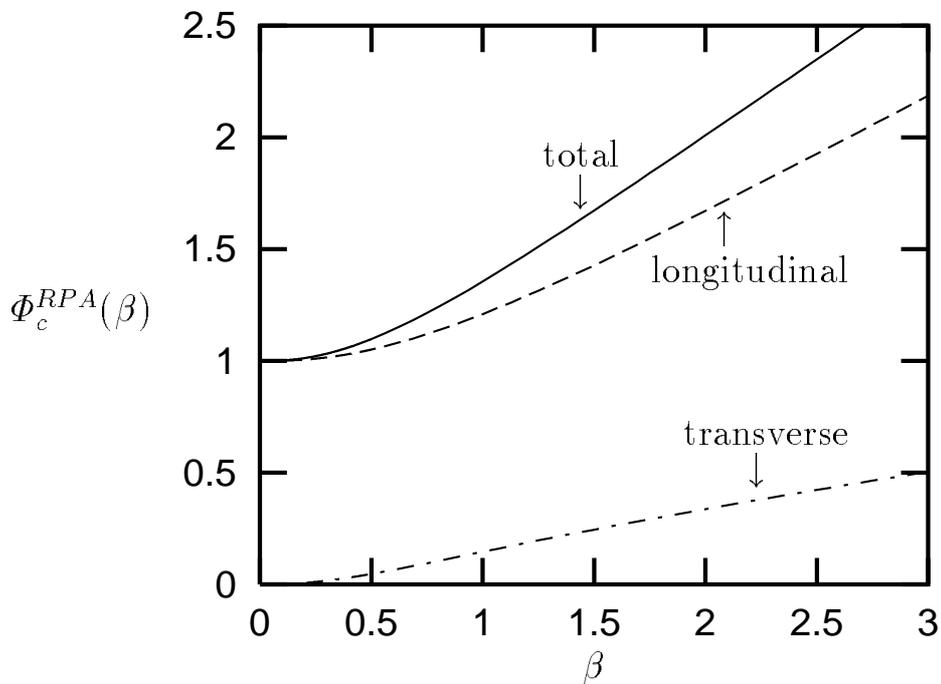


Fig. 4.4. Relativistic corrections to the LDA correlation energy density within the RPA [99].

the RPA to e_c^{RHEG} is substantial (a similar correction factor is found for the corresponding correlation potential [22, 98]).

One may ask whether the correction factor Φ_c^{RPA} , Eq.(4.7), can be of any use in actual applications. In this respect it is important to note that for the nonrelativistic HEG the RPA, which only contains one of the diagrammatic contributions to e_c^{NRHEG} of order e^4 , is not an accurate approximation to the full e_c^{NRHEG} even for the highest relevant densities inside the nuclei of high- Z atoms ($\beta \approx 10 \Leftrightarrow r_s \approx 0.001$). On the other hand, the combination of $e_c^{RHEG,RPA}$ with the remaining contributions of order e^4 (here abbreviated by RPA+) agrees within an accuracy of 3% with e_c^{NRHEG} already for densities

with $r_s \approx 0.1$ ($\beta \approx 0.1$), i.e. for densities below which relativistic corrections are irrelevant (note that all relativistic corrections are proportional to β^2 for small β). Consequently in this intermediate and low density regime the well known nonrelativistic e_c^{NRHEG} can also be used for the RLDA. An accurate form for the RLDA correlation energy is thus obtained from

$$e_c^{RHEG}(n) = e_c^{RHEG,RPA+}(n) - e_c^{NRHEG,RPA+}(n) + e_c^{NRHEG}(n) , \quad (4.8)$$

where the relativistic corrections are only included via the RPA+ (which also dominates in the relativistic high-density limit — compare Appendix B.). For low and intermediate densities $e_c^{RHEG,RPA+}(n)$ and $e_c^{NRHEG,RPA+}(n)$ cancel each other, while for relativistic densities higher than $\beta \approx 0.1$ the two right-most expressions cancel. Unfortunately, the complete density dependence of the relativistic RPA+ is not known. In the high density limit, however, one finds [96]

$$e_c^{RHEG,RPA+}(n) \underset{\beta \gg 1}{\approx} 1.4 e_c^{RHEG,RPA}(n) , \quad (4.9)$$

so that $\Phi_c^{RPA}(n)$ represents a lower bound for the total $\Phi_c(n)$. The error for the relevant density range $0.1 < \beta < 1$ is difficult to estimate, but should be less than the 30% indicated by (4.9) as on the nonrelativistic level $e_c^{NRHEG,RPA+}$ and $e_c^{NRHEG,RPA}$ differ by roughly 20% for $\beta = 0.1$. In view of the fact that the RPA+ has not been fully evaluated, however, only the relativistic correction due to the RPA can presently be used instead of the more accurate form (4.8),

$$e_c^{RHEG}(n) \simeq e_c^{RHEG,RPA}(n) - e_c^{NRHEG,RPA}(n) + e_c^{NRHEG}(n) . \quad (4.10)$$

4.2 Relativistic Weighted Density Approximation

In the nonrelativistic LDA one finds partial, but by no means satisfactory cancellation of self interaction effects between E_H and E_x^{LDA} . The WDA [100, 101] constitutes a relatively direct approach, in which one attempts to improve on this situation by a density functional representation of the pair correlation function.

In order to apply the WDA in the relativistic regime, a fully covariant extension of the concept of the pair correlation function would be desirable. To our knowledge this is, however, not available. Nevertheless, if one restricts the discussion to the (instantaneous) longitudinal limit, one can express $E_{xc}^L[n]$, Eq.(3.21), via a relativistic pair correlation function defined in analogy to the nonrelativistic case as

$$g(\mathbf{r}, \mathbf{r}') = \frac{\langle \Phi_0 | \hat{n}(\mathbf{r}) \hat{n}(\mathbf{r}') | \Phi_0 \rangle}{n(\mathbf{r}) n(\mathbf{r}')} - \frac{\delta^{(3)}(\mathbf{r} - \mathbf{r}')}{n(\mathbf{r})} . \quad (4.11)$$

By definition, g is symmetric,

$$g(\mathbf{r}, \mathbf{r}') = g(\mathbf{r}', \mathbf{r}) , \quad (4.12)$$

and satisfies the sum rule

$$\int d^3 r' n(\mathbf{r}') [g(\mathbf{r}, \mathbf{r}') - 1] = -1. \quad (4.13)$$

In fact, (4.13) is also satisfied by the x-only limit g_x of g , i.e. its lowest order contribution in e^2 . In the relativistic case only this limit of the pair correlation function of the RHEG, $g_x^{RHEG}(k_F |\mathbf{r} - \mathbf{r}'|, k_F)$, specified in Eq.(B.68), is known (within the no-pair approximation [19, 102]), so that we restrict the subsequent discussion to the x-only limit.

For the transition from the x-only RLDA to the x-only RWDA one replaces the constant k_F inside $g_x^{RHEG}(k_F |\mathbf{r} - \mathbf{r}'|, k_F)$ by a local screening momentum $\tilde{k}_F(\mathbf{r})$, which is determined by the requirement, that the basic sum rule (4.13) be satisfied in the form

$$\int d^3 r' n(\mathbf{r}') [g_x^{RHEG}(\tilde{k}_F(\mathbf{r}) |\mathbf{r} - \mathbf{r}'|, \tilde{k}_F(\mathbf{r})) - 1] = -1 \quad (4.14)$$

for any given \mathbf{r} . One should note that this prescription leads to a truly non-local functional,

$$E_x^{L,RWDA}[n] = \frac{e^2}{2} \int d^3 r \int d^3 r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \times [g_x^{RHEG}(\tilde{k}_F(\mathbf{r}) |\mathbf{r} - \mathbf{r}'|, \tilde{k}_F(\mathbf{r})) - 1], \quad (4.15)$$

but violates the general symmetry (4.12) so that one obtains different x-only potentials depending on whether the WDA scheme is applied before or after variation with respect to the density. Moreover, using g_x^{RHEG} as a kernel the x-only RWDA reduces to a pure density functional, without any \mathbf{j} -dependence.

The main advantage of this approximation is that it is exact for two-electron systems (if the correct $\tilde{k}_F(\mathbf{r}) = 0$ is utilised in (4.15) before performing the functional differentiation (3.17) required for its application) and also correctly accounts for the self interaction energies of individual closed shells if a shell-partitioning scheme is used [71]. Furthermore, the RWDA reproduces the asymptotic r^{-1} proportionality of the exact x-only potential (although with the incorrect prefactor of 1/2 [103]).

5. Relativistic DFT Results for Atoms

So far only few applications of the RKS-equations (3.25-3.29) utilising a relativistic form for $E_{xc}[n]$ have been reported (and none for the 'field theoretical' KS-equations (3.5,3.15-3.17)). MacDonald and Vosko [19] as well as Das et al. [104] analysed the x-only RLDA for high- Z atoms and ions, emphasising the importance of relativistic corrections to $E_x[n]$. This work has been extended by inclusion of the RPA limit of $E_c[n]$ in the RLDA by Ramana et

al. [97]. These authors also point out the need for nonlocal corrections, in particular in the case of the x-only energy. The influence of relativistic corrections to $E_{xc}[n]$ on the band structures of Pd and Pt has been examined by MacDonald et al. [105], who find a significant effect on the Fermi surface of Pt. In particular, they conclude that relativistic corrections to $v_x[n]$ can be as important as the nonrelativistic $v_c[n]$ even for the valence levels of high- Z systems.

On the other hand, a large number of relativistic Slater calculations [23] (Dirac-Fock-Slater — DFS), in which the RKS-equations are used with the nonrelativistic x-only LDA, can be found in the literature (see e.g.[8, 9]). However, no attempt is made to review this extensive body of literature here.

In this Section we summarise the properties of the approximations to $E_{xc}[n]$ discussed in Section 4. in applications to atoms. All results presented in the following [36] are based on the direct numerical solution of Eqs.(3.25-3.29) using a nuclear potential which corresponds to a homogeneously charged sphere [69]¹³. Only spherical, i.e. closed subshell, atoms and ions are considered. Whenever suitable we use Hg as a prototype of all high- Z atoms.

In the following we investigate both the importance of relativistic corrections to $E_{xc}[n]$ and the adequacy of the RLDA and RWDA to reproduce them, using ROPM and conventional relativistic *ab initio* results as reference standards. Consequently it is not so much the accuracy of the total relativistic xc-energies which is of interest, but rather their intrinsically relativistic ingredients, i.e. the differences between the selfconsistent relativistic and the selfconsistent nonrelativistic longitudinal xc-energies,

$$\Delta E_{x,c}^L = E_{x,c}^L[n^R] - E_{x,c}^{NR}[n^{NR}] \quad (5.1)$$

and the transverse xc-energies $E_{x,c}^T$. Here n^R represents the selfconsistent density obtained by solving the RKS-equations with a given (approximate) form for $E_{x,c}^L[n]$. Its nonrelativistic counterpart n^{NR} is obtained by solution of the nonrelativistic KS-equations with the nonrelativistic limit $E_{x,c}^{NR}[n]$ of $E_{x,c}^L[n]$. In the x-only limit one can examine relativistic corrections on a local level via

$$\Delta v_x^L(r) = \frac{v_x^L([n^R]; r) - v_x^{NR}([n^{NR}]; r)}{v_x^{NR\text{OPM}}([n^{NR\text{OPM}}]; r)} \quad (5.2)$$

Δv_x^L represents the percentage deviation of the selfconsistent relativistic potential $v_x^L([n^R]; r)$ from the corresponding selfconsistent nonrelativistic potential $v_x^{NR}([n^{NR}]; r)$. The selfconsistent $v_x^L([n^R]; r)$ is calculated by insertion of the selfconsistent $n^R(r)$ into the functional derivative (3.28) for that $E_x^L[n]$ which has been used to determine $n^R(r)$. In particular, the ROPM x-only potential can, in principle, be obtained by insertion of the exact x-only density

¹³ All our calculations have been performed without a Latter type correction for $v_x(r)$ in the large- r regime (compare [104]).

$n^{ROPM}(r)$ into the exact $v_x^L([n]; r) = v_x^{ROPM}([n]; r)$ and thus can be used as a comparative standard: $\Delta v_x^{L,ROPM}(r)$ constitutes a direct local measure of relativistic corrections in the x-only limit with which $\Delta v_x^L(r)$ from various approximations can be compared (for the corresponding deviations of approximate $v_x^{NR}(r)$ from $v_x^{NROPM}(r)$ see [59, 60, 106]).

5.1 Longitudinal x-only Functionals

Before considering approximations to the exact $E_x^L[n]$, Eq.(3.37), some general remarks on the importance of relativistic corrections on the ROPM-level seem appropriate. First of all one gleans from Table 5.1 that the relativistic contributions in E_x^L are quite substantial: For instance for Hg one obtains a *20hartree* shift when going from the nonrelativistic OPM- to the ROPM-value which represents 5.8% of E_x^L , very similar to the 6.8% relativistic correction which is found for E_{tot}^L . Clearly, relativistic effects are most important

Table 5.1. Longitudinal (Coulomb) x-only energies ($-E_x^L$) for closed subshell atoms from NROPM-, ROPM-, RHF-, DFS-, RLDA-, and RWDA-calculations [36, 69] (all energies are in *hartree*).

Atom	NROPM	ROPM	RHF	DFS	RLDA	RWDA
He	1.026	1.026	1.026	0.853	0.853	1.026
Be	2.666	2.667	2.668	2.278	2.278	2.706
Ne	12.105	12.120	12.123	10.952	10.944	12.843
Mg	15.988	16.017	16.023	14.564	14.550	17.093
Ar	30.175	30.293	30.303	27.897	27.844	32.419
Ca	35.199	35.371	35.383	32.702	32.627	37.967
Zn	69.619	70.245	70.269	66.107	65.834	75.604
Kr	93.833	95.048	95.072	89.784	89.293	102.095
Sr	101.926	103.404	103.429	97.836	97.251	111.133
Pd	139.113	141.898	141.930	134.971	133.887	152.275
Cd	148.879	152.143	152.181	144.931	143.687	163.321
Xe	179.062	184.083	184.120	175.926	174.102	197.564
Ba	189.065	194.804	194.841	186.417	184.363	209.171
Yb	276.143	288.186	288.265	278.642	274.386	310.268
Hg	345.240	365.203	365.277	354.299	347.612	392.339
Rn	387.445	414.082	414.151	402.713	394.102	444.584
Ra	401.356	430.597	430.664	419.218	409.871	462.365
No	511.906	564.309	564.415	554.242	538.040	606.216

for the innermost orbitals. This is obvious from Table 5.2 showing the single particle spectrum of Hg. Note that the $2P_{1/2}$ -eigenvalue is modified by 17% and that even the outermost $6S_{1/2}$ -eigenvalue experiences a 26% shift (reflecting the 'gold maximum'). Table 5.2 also demonstrates that apart from the physically relevant highest occupied eigenvalue and in spite of the very similar ground state energies ROPM and RHF single particle energies differ substantially (compare [59]), in consistency with their auxiliary character.

Table 5.2. Single particle energies ($-\epsilon_{nlj}$) for Hg from NROPM-, ROPM- and RHF-calculations in comparison with DFS-, RLDA- and RWDA-results (all energies are in *hartree*).

Level	NROPM	ROPM	RHF	DFS	RLDA	RWDA
1S1/2	2756.925	3047.430	3074.228	3047.517	3044.410	3051.995
2S1/2	461.647	540.056	550.251	539.713	539.250	540.530
2P1/2	444.015	518.061	526.855	518.164	517.746	519.244
2P3/2	444.015	446.682	455.157	446.671	446.399	447.469
3S1/2	108.762	128.272	133.113	128.001	127.905	128.292
3P1/2	100.430	118.350	122.639	118.228	118.148	118.592
3P3/2	100.430	102.537	106.545	102.397	102.346	102.691
3D3/2	84.914	86.201	89.437	86.085	86.060	86.364
3D5/2	84.914	82.807	86.020	82.690	82.668	82.959
4S1/2	23.522	28.427	30.648	28.067	28.046	28.200
4P1/2	19.895	24.161	26.124	23.871	23.854	24.023
4P3/2	19.895	20.363	22.189	20.039	20.030	20.167
4D3/2	13.222	13.411	14.797	13.148	13.146	13.271
4D5/2	13.222	12.700	14.053	12.434	12.432	12.553
4F5/2	4.250	3.756	4.473	3.556	3.559	3.665
4F7/2	4.250	3.602	4.312	3.402	3.404	3.509
5S1/2	3.501	4.403	5.103	4.290	4.286	4.349
5P1/2	2.344	3.012	3.538	2.898	2.896	2.955
5P3/2	2.344	2.363	2.842	2.219	2.218	2.265
5D3/2	0.538	0.505	0.650	0.363	0.363	0.397
5D5/2	0.538	0.439	0.575	0.296	0.296	0.328
6S1/2	0.262	0.329	0.328	0.222	0.222	0.254

The percentage relativistic contribution in the exact v_x^L is plotted in Fig.5.1. One clearly observes an 'oscillatory' behavior between $0.01a.u.$ and $3a.u.$ reflecting the shell structure of the atom: Most relativistic single particle orbitals are shifted towards the nucleus with respect to the nonrelativistic ones¹⁴, resulting in an oscillating structure of $n^R(r) - n^{NR}(r)$ and thus also of Δv_x^L . This leads to an additional attraction of about 20% in the region close to the nucleus. Even in the valence regime the relativistic correction amounts to roughly 10%.

In view of these results there is little doubt that the density dependence of explicit density functionals for the x-only energy has to be modified in the relativistic regime.

On the basis of exact OPM results one can now examine approximate forms for $E_x^L[n]$. Here we consider the two relativistic functionals available, i.e. the RLDA and the RWDA¹⁵ discussed in Section 4., as well as the nonrela-

¹⁴ All $S1/2$ and $P1/2$ orbitals are considerably contracted, the $P3/2$, $3D3/2$ and $4D3/2$ orbitals only slightly. While the $5D3/2$ as well as the $3D5/2$ and $4D5/2$ r -expectation values remain essentially unchanged, the $5D5/2$, $4F5/2$ and $4F7/2$ orbitals are expanded.

¹⁵ All numerical results from the RWDA have been obtained with the fit (B.73) to the exact pair correlation function.

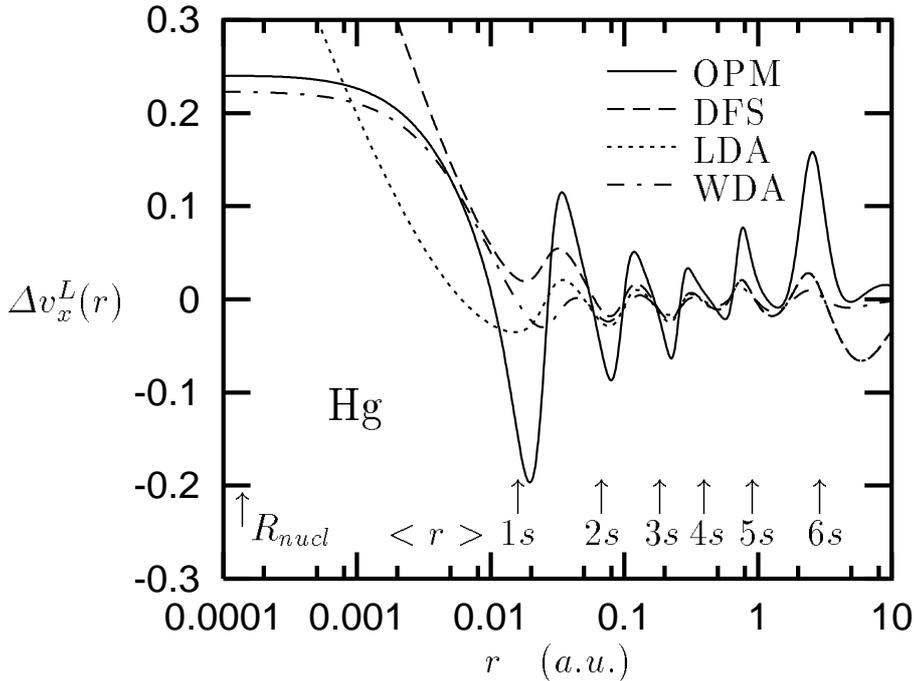


Fig. 5.1. Percentage relativistic correction to the longitudinal x-only potential $\Delta v_x^L(r)$, Eq.(5.2), for neutral Hg from OPM-, DFS-, LDA- and WDA-calculations [69]. Also shown are the nuclear radius R_{nucl} and the r -expectation values of the individual s -orbitals.

tivistic LDA (NRLDA), i.e. the DFS-approach with $\alpha = 2/3$. For comparison with the ROPM-results in Table 3.1 the corresponding longitudinal x-only ground state energies and highest occupied eigenvalues are listed in Table 5.3. Two features are apparent from this comparison: On the one hand, the total ground state energies of all three approximations differ considerably from the corresponding ROPM values (in Table 3.1). While the RWDA overestimates the binding energy substantially, both the RLDA and the DFS energies are too small. This deviation can be directly traced to the corresponding E_x^L (given in Table 5.1): For instance for Hg the error of 17.204 hartree for E_{tot}^L matches rather well with the corresponding error of 17.591 hartree for E_x^L . The same holds for the DFS- and RWDA-results (and throughout the periodic table).

On the other hand, the highest occupied eigenvalues which reflect the asymptotic form of the density, and thus even in the x-only limit should be close to the ionisation potential, are too small by roughly 50% for the DFS and RLDA and by 30-40% for the RWDA¹⁶. Thus while the latter improves on the asymptotic form of v_x^L in principle, the effect of this formal improvement on the physically relevant part of the asymptotic regime is rather limited. Note

¹⁶ For He the selfconsistent RWDA-potential has also been evaluated by insertion of \tilde{k}_F into the complete functional derivative of (4.15).

Table 5.3. Longitudinal x-only ground state energies ($-E_{tot}^L$) and highest occupied eigenvalues ($-\epsilon_{mk}^L$) for closed subshell atoms from DFS, RLDA and RWDA calculations [36] (all energies are in *hartree*). Note that for Yb the DFS-, RLDA- and RWDA-calculations incorrectly predict the 4F7/2-orbital to be most weakly bound. The values given (*), however, correspond to the 6S1/2-orbital.

Atom	$-E_{tot}^L$			$-\epsilon_{mk}^L$		
	DFS	RLDA	RWDA	DFS	RLDA	RWDA
He (1S1/2)	2.724	2.724	2.862	0.517	0.517	0.599
Be (2S1/2)	14.226	14.226	14.609	0.170	0.170	0.204
Ne (2P3/2)	127.635	127.628	129.417	0.441	0.441	0.511
Mg (3S1/2)	198.569	198.556	200.963	0.142	0.142	0.181
Ar (3P3/2)	526.387	526.337	530.747	0.331	0.331	0.369
Ca (4S1/2)	677.118	677.047	682.204	0.112	0.112	0.140
Zn (4S1/2)	1790.721	1790.458	1799.949	0.191	0.191	0.232
Kr (4P3/2)	2783.758	2783.282	2795.778	0.291	0.291	0.321
Sr (5S1/2)	3172.638	3172.071	3185.631	0.104	0.104	0.129
Pd (4D5/2)	5037.733	5036.677	5054.707	0.111	0.111	0.151
Cd (5S1/2)	5586.299	5585.086	5604.337	0.181	0.181	0.218
Xe (5P3/2)	7438.858	7437.076	7460.124	0.250	0.250	0.275
Ba (6S1/2)	8127.344	8125.336	8149.714	0.095	0.095	0.116
Yb (6S1/2)	14058.528	14054.349	14089.603	0.119*	0.119*	0.146*
Hg (6S1/2)	19638.195	19631.622	19675.706	0.222	0.222	0.254
Rn (6P3/2)	23590.763	23582.293	23632.105	0.214	0.214	0.237
Ra (7S1/2)	25016.763	25007.568	25059.377	0.097	0.097	0.117
No (7S1/2)	36730.804	36714.839	36782.219	0.128	0.128	0.156

further, that for Yb all three schemes incorrectly predict the 4F7/2-orbital to be most weakly bound instead of the 6S1/2-orbital. The same deficiency has been observed for Cr and Cu in the nonrelativistic case [59]. These difficulties to reproduce the size and the ordering of the outermost eigenvalues are well known from the nonrelativistic case and are not related to the relativistic corrections in $E_x^L[n]$.

The percentage deviation of the relativistic correction ΔE_x^L , Eq.(5.1), obtained for the three approximations with respect to the OPM standard is plotted in Fig.5.2. While both the DFS and the WDA overestimate the exact ΔE_x^L by about 10%, the LDA underestimates them by roughly 20% in the relevant Z -regime. One notes, however, that the deviation of the LDA seems to be decreasing with increasing Z in contrast to the errors of the DFS and the WDA. In any case, all three approximations are not satisfactory from a quantitative point of view.

The fact that the longitudinal x-only energies obtained from some approximate functional are rather insensitive to the density inserted into the functional [19] is demonstrated explicitly in Table 5.4. Here the E_x^L obtained by insertion of the selfconsistent ROPM-, DFS-, RLDA-, and RWDA-densities

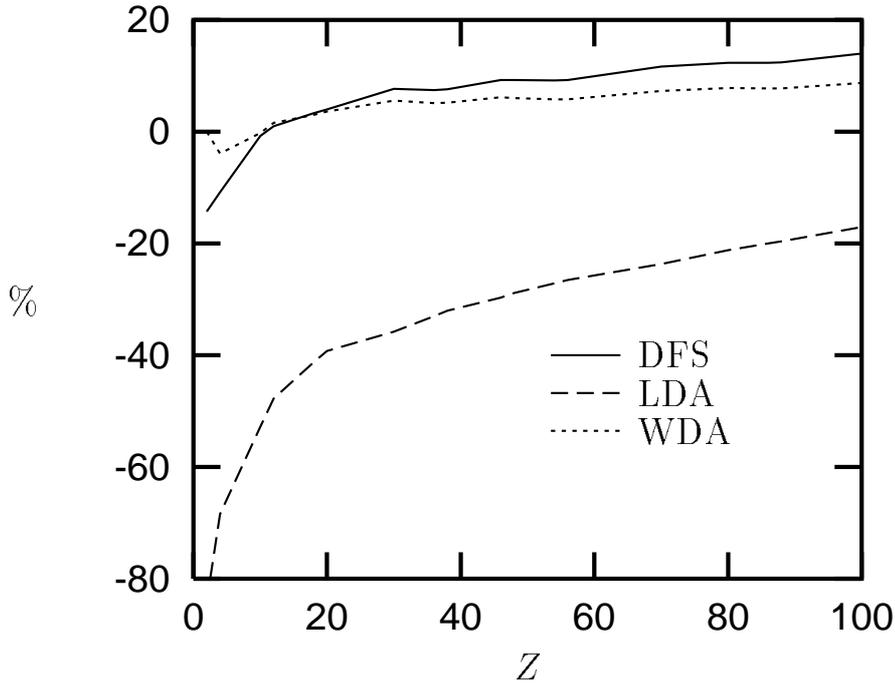


Fig. 5.2. Percentage deviation of ΔE_x^L for neutral atoms with respect to the exact OPM results obtained from DFS, LDA and WDA.

for Hg into the corresponding functionals are listed¹⁷: While the energy differences between the four functionals (for any given density) are substantial, the differences generated by the four densities for a given functional are of the order of a few 100mhartree . These latter differences originate from the selfconsistency procedure, i.e. from the corresponding v_x^L . In other words: The selfconsistent n^R is dominated by relativistic kinematics and the nuclear attraction, the x-potential only plays a minor role. Nevertheless the impact of the relativistic corrections in v_x^L on atomic exchange energies is larger than the differences between more refined nonlocal functionals on the nonrelativistic level. Consequently relativistic corrections to the longitudinal x-only energy should not just be taken into account perturbatively, but rather be included in the selfconsistency loop.

The relativistic corrections in v_x^L are also apparent for the innermost RKS-eigenvalues. Notwithstanding their auxiliary nature, these single particle levels are a direct measure of the quality of any approximation to the relativistic $v_x^L[n]$. Focussing on the 1S_{1/2}-eigenvalue of Hg Table 5.2 shows that the values for both the RLDA and the RWDA deviate by several *hartree* from the ROPM eigenvalue, indicating that $v_x^{L,RLDA}$ is not sufficiently attractive, while $v_x^{L,RWDA}$ overestimates the actual ROPM-potential. The in-

¹⁷ Note that insertion of a given density into the exact x-only functional corresponds to insertion of the RKS-orbitals which yield this density into (3.37).

Table 5.4. Longitudinal (Coulomb) exchange energies ($-E_x^L$) for Hg obtained by insertion of selfconsistent ROPM-, DFS-, RLDA- and RWDA-densities into the corresponding $E_x^L[n]$ (all energies are in *hartree*).

Hg $E_x^L[n]$	Densities from			
ROPM	DFS	RLDA	RWDA	
ROPM	365.203	364.865	364.745	365.366
DFS	354.508	354.299	354.181	354.805
RLDA	347.928	347.722	347.612	348.216
RWDA	391.988	391.785	391.656	392.339

nermost DFS-eigenvalues, on the other hand, seem to agree rather well with the ROPM-results, which, however, must be regarded as fortuitous.

This last point is emphasised if one looks at the relativistic correction to the x-only potential, Δv_x^L , shown for Hg in Fig.5.1. While the shell oscillations of the exact v_x^L are at least partially reproduced by all three approximations (the OPM-amplitudes being larger by more than a factor of 2), both the DFS- and the RLDA-potentials are far from the exact $\Delta v_x^L(r)$ in the region close to the nucleus. For these approximations v_x^L is proportional to $n^{1/3}$ for high densities [19], with the prefactor being larger for DFS. In spite of the fact that we use extended nuclei this proportionality starts to show up at about the r -expectation value of the 1S1/2-orbital. On the other hand, the RWDA follows the exact $\Delta v_x^L(r)$ rather closely in the small- r regime. This can be understood from the fact that this part of $v_x^L(r)$ is dominated by the self interaction correction of the 1S1/2-orbital, for which the RWDA-concept is particularly suitable. This result suggests to search for a relativistic extension of the model pair correlation functions which are more accurate than $g_x^{(R)HEG}$ in the nonrelativistic regime [36, 100].

In order to analyse the origin of the failure of the RLDA it is useful to separate the two effects leading to the relativistic correction in the x-only energies [36],

$$\Delta E_x^L = \Delta E_x(dens) + \Delta E_x(ctl) \quad (5.3)$$

$$\Delta E_x(dens) = E_x^{NR}[n^R] - E_x^{NR}[n^{NR}] \quad (5.4)$$

$$\Delta E_x(ctl) = E_x^L[n^R] - E_x^{NR}[n^R] , \quad (5.5)$$

i.e. the correction $E_x^{NR}[n^R] - E_x^{NR}[n^{NR}]$ resulting from the difference between the selfconsistent relativistic density n^R and the selfconsistent non-relativistic density n^{NR} and the contribution $E_x^L[n^R] - E_x^{NR}[n^R]$ arising from the relativistic modification of the functional form of the x-only functional. Using the LDA one finds for Hg $\Delta E_x(dens) = -22.303\text{hartree}$ and $\Delta E_x(ctl) = 6.569\text{hartree}$. Thus the dominating density contribution increases the x-only energy, while the functional correction leads to a reduction (as is immediately obvious from Φ_x^L , Fig.4.1) and both are of the same order of magnitude. Moreover, $\Delta E_x(dens)$ is rather insensitive to the precise

form of $E_x^L[n]$ due to the insensitivity of n^R to v_x^L noted earlier. For instance the values of $\Delta E_x(dens)$ from the LDA are almost identical with the complete ΔE_x^L from the DFS approach ($-22.421hartree$ for Hg). $\Delta E_x(fctl)$, on the other hand, is exclusively determined by the form of $E_x^L[n]$. The need to balance the contributions $\Delta E_x(dens)$ and $\Delta E_x(fctl)$ becomes even more obvious if a more accurate nonrelativistic $E_x^{NR}[n]$ like a GGA is used: For Hg Becke's GGA [10] (applied without any functional correction) yields $\Delta E_x^L = \Delta E_x(dens) = 24.978hartree$ which overshoots the exact value by $5.015hartree$ to be compensated by $\Delta E_x(fctl)$.

For an evaluation of the exact $\Delta E_x(dens)$ and $\Delta E_x(fctl)$ one needs the set of nonrelativistic KS-orbitals which generates the ROPM density (required for $E_x^{NR}[n^R]$). While the calculation of these orbitals is a rather complicated task and thus will not be addressed here, there is one type of system for which the exact $\Delta E_x(dens)$ is identical with the complete ΔE_x^L as the functional contribution $\Delta E_x(fctl)$ vanishes: For all two-electron systems the exact $E_x^L[n]$,

$$E_x^L[n] = -\frac{e^2}{4} \int d^3r \int d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} , \quad (5.6)$$

is identical with the exact $E_x^{NR}[n]$. The OPM values for Hg⁷⁸⁺ can thus be compared with the corresponding LDA results,

$$\begin{aligned} \Delta E_x^{OPM}(dens) &= -7.963hartree \quad , \quad \Delta E_x^{OPM}(fctl) = 0 \\ \Delta E_x^{LDA}(dens) &= -7.198hartree \quad , \quad \Delta E_x^{LDA}(fctl) = 3.157hartree . \end{aligned}$$

The error of $765mhartree$ for $\Delta E_x(dens)$ reflects the fact that the LDA is missing important nonlocal contributions responsible for the cancellation of the self interaction energy already on the nonrelativistic level. The much larger LDA error for $\Delta E_x(fctl)$, on the other hand, directly shows that nonlocal corrections are even more relevant for the relativistic correction $E_x^L[n^R] - E_x^{NR}[n^R]$. Furthermore, the total deviation of $3.922hartree$ in the LDA found for Hg⁷⁸⁺ agrees rather well with the deviation of $4.229hartree$ for neutral Hg, suggesting that the major contribution to ΔE_x^L comes from the $1S1/2$ -electrons, while contributions of the order of $300mhartree$ are due to the relativistic rearrangement of other orbitals.

The last point becomes more transparent if one decomposes $\Delta v_x^L(r)$ into its density and functional components (in analogy to Eqs.(5.3-5.5)),

$$\Delta v_x^L(r) = \Delta v_x(r, dens) + \Delta v_x(r, fctl) \quad (5.7)$$

$$\Delta v_x(r, dens) = \frac{v_x^{NR}([n^R]; r) - v_x^{NR}([n^{NR}]; r)}{v_x^{NROPM}([n^{NROPM}]; r)} \quad (5.8)$$

$$\Delta v_x(r, fctl) = \frac{v_x^L([n^R]; r) - v_x^{NR}([n^R]; r)}{v_x^{NROPM}([n^{NROPM}]; r)} . \quad (5.9)$$

One finds that the oscillatory structure of $\Delta v_x^L(r)$ observed in Fig.5.1 is completely due to the density correction $\Delta v_x(r, dens)$, as can be gleaned

from Fig.5.3¹⁸. As expected, the functional correction $\Delta v_x(r, fctl)$ is only

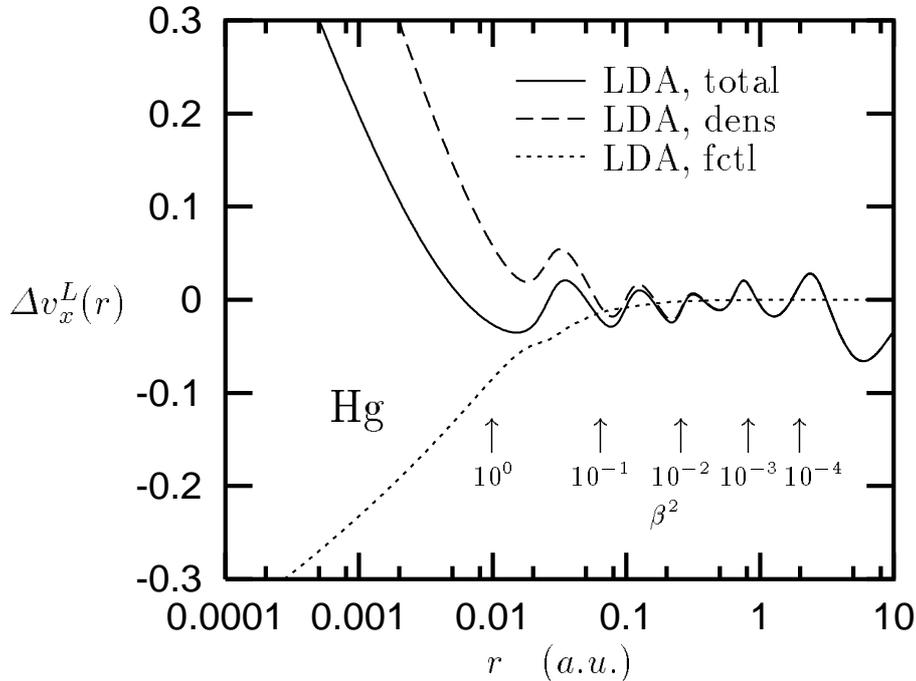


Fig. 5.3. Decomposition of Δv_x^L (total) into its density component (5.8) (dens) and the functional contribution (5.9) (fctl): LDA-results for neutral Hg. Also shown are some characteristic β^2 -values.

relevant for the high density small- r regime, i.e. the innermost orbitals. In this regime, however, the $\Delta v_x^L(r)$ from the LDA is rather different from the exact OPM result. In order to demonstrate that both components of $\Delta v_x^L(r)$ contribute to the error of the LDA it is again advantageous to consider Hg^{78+} : Similar to the situation for ΔE_x^L the exact $\Delta v_x(r, fctl)$ vanishes. As is clear from Fig.5.4 the LDA does not reproduce the exact $\Delta v_x^L(r)$. In particular, $|\Delta v_x^{LDA}(r, fctl)|$ does not vanish but is of the same order of magnitude as the exact $\Delta v_x(r, dens)$.

Consequently the origin of the failure of the RLDA for neutral atoms is twofold: The error is dominated by the self interaction of the $1S_{1/2}$ -electrons which manifests itself mainly in the functional correction $E_x^L[n] - E_x^{NR}[n]$. The smaller (but chemically equally relevant) error in the density components $\Delta E_x(dens)$ and $\Delta v_x(r, dens)$, on the other hand, is a result of the difficulties of the LDA to reproduce the shell structure of the exact density already in the nonrelativistic regime [59, 106]: The amplitude (not the location) of the relativistic shift of the individual shells becomes larger if the shells are more

¹⁸ The LDA-result for $\Delta v_x(r, dens)$ is almost identical with the complete selfconsistent $\Delta v_x^L(r)$ from the DFS-scheme.

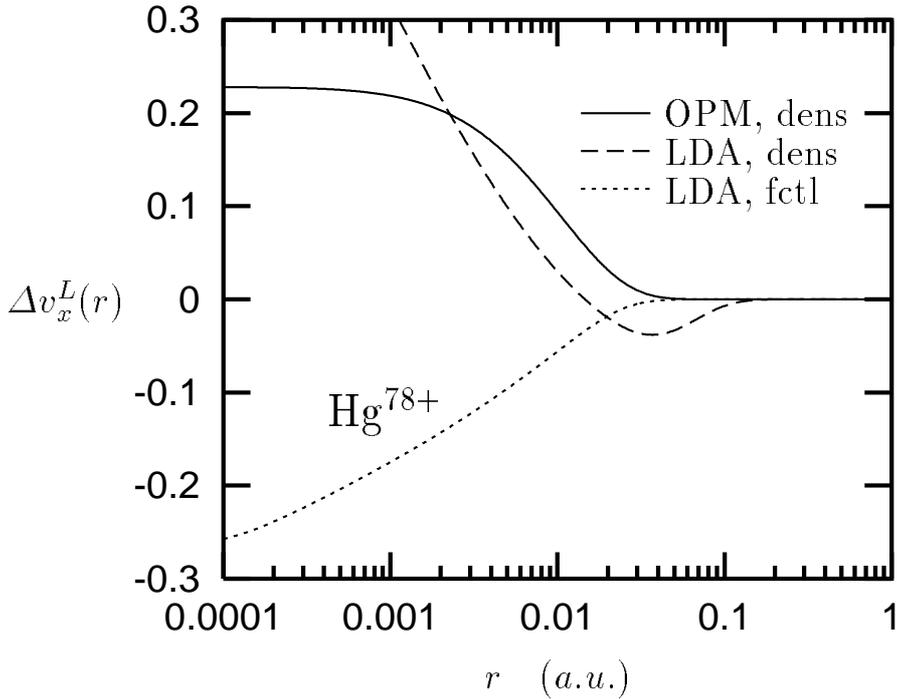


Fig. 5.4. Decomposition of $\Delta v_x^L(r)$ for Hg^{78+} : Exact $\Delta v_x(r, dens)$ (OPM,dens) in comparison with $\Delta v_x^{LDA}(r, dens)$ (LDA,dens) and $\Delta v_x^{LDA}(r, fctl)$ (LDA,fctl).

pronounced. While the first source of errors calls for improved, i.e. nonlocal, relativistic corrections to the x-only energy functional, the second problem can only be resolved by using a more accurate nonrelativistic starting point for $E_x^L[n]$ than the NRLDA.

5.2 Relativistic LDA for $E_x^T[n]$

We now turn to a brief discussion of the RLDA for $E_x^T[n]$, which is the only density functional approximation for this quantity available to date. The transverse x-only energies calculated from the selfconsistent RLDA densities are compared with RHF results [68, 48] in Table 5.5. The RHF orbitals used for these energies [68] could be replaced by the ROPM or RLDA orbitals without significantly changing the resulting E_x^T 's: For Hg e.g. one obtains 22.145 *hartree* by inserting the selfconsistent RLDA-orbitals into the transverse Fock term. As pointed out by MacDonald and Vosko [19] the RLDA overestimates the exact E_x^T by about a factor of 1.5. Moreover, in contrast to the RLDA's error for ΔE_x^L the error for E_x^T does not decrease with increasing Z . Thus the RLDA can only serve as a qualitative measure of transverse x-only energies. Furthermore, the rather subtle cancellation observed for the exact ΔE_x^L and E_x^T is not found in the RLDA. The RLDA thus completely misrepresents the total relativistic correction to atomic exchange energies [36] (see Table 5.5).

Table 5.5. Transverse exchange energies (E_x^T) and its Breit approximation ($E_x^{T,Breit}$) from RHF- [68] and RLDA-calculations [36]. Also the total correction $\Delta E_x^L + E_x^T$ is given (all energies are in *hartree*).

Atom	RHF			RLDA		
	E_x^T	$E_x^{T,Breit}$	$\Delta E_x^L + E_x^T$	E_x^T	$E_x^{T,Breit}$	$\Delta E_x^L + E_x^T$
He	0.000	0.000	0.000	0.000	0.000	0.000
Be	0.001	0.001	0.000	0.002	0.002	0.001
Ne	0.017	0.017	0.002	0.035	0.035	0.028
Mg	0.032	0.032	0.003	0.065	0.064	0.050
Ar	0.132	0.132	0.014	0.249	0.248	0.180
Ca	0.191	0.191	0.019	0.353	0.352	0.249
Zn	0.759	0.761	0.131	1.322	1.312	0.920
Kr	1.419	1.427	0.203	2.401	2.373	1.586
Sr	1.710	1.720	0.231	2.867	2.831	1.862
Pd	3.290	3.318	0.503	5.358	5.263	3.399
Cd	3.808	3.842	0.541	6.162	6.045	3.840
Xe	5.711	5.775	0.687	9.089	8.877	5.431
Ba	6.473	6.552	0.733	10.255	10.001	6.038
Yb	13.897	14.148	1.846	21.557	20.778	12.355
Hg	22.166	22.665	2.192	34.201	32.654	18.444
Rn	28.676	29.397	2.028	44.313	42.046	22.964
Ra	31.148	31.957	1.899	48.202	45.636	24.638
No	53.576	55.248	1.154	84.987	79.083	41.085

As is well known the Breit approximation to E_x^T is rather close to the full E_x^T throughout the periodic table for both RHF [48] and the RLDA [97]. Taking into account the subtle cancellation between E_x^T and ΔE_x^L , however, the difference between E_x^T and $E_x^{T,Breit}$ amounts to an appreciable percentage of the total $\Delta E_x^L + E_x^T$, at least for high- Z atoms. Furthermore, the RLDA for the Breit approximation leads to energies smaller than the $E_x^{T,RLDA}$ in contrast to the correct relationship. Thus while the error of the RLDA for ΔE_x^L , i.e. in the nonrelativistic (Coulomb) limit of the full photon exchange, is roughly 20%, it increases to about 50% for $E_x^{T,Breit}$, i.e. the first order weakly relativistic correction to the Coulomb interaction, and finally the RLDA even misses the correct sign for $E_x^T - E_x^{T,Breit}$, i.e. all higher order relativistic corrections to the Coulomb interaction.

The failure of the RLDA for $E_x^T[n]$ is, however, not surprising in view of its RHEG origin. The finite speed of light plays a much more important role for an infinite system like the RHEG than for atoms: In the RHEG extremely distant points in space are interacting with each other so that the travelling time of photons between these points modifies the form of the long range electromagnetic forces (similar to the difference between Casimir-Polder and van der Waals forces [26]). The electronic density of atoms, on the other hand, is rather localised so that the actual propagation of photons as compared with the instantaneous Coulomb interaction can not have the same impact.

5.3 Relativistic LDA for $E_c[n]$

Our review of the properties of explicit relativistic functionals is concluded by an examination of the RLDA for $E_c[n]$ (using the RPA for the relativistic corrections, Eq.(4.10), and the parametrisation of Vosko et al. [70] for $e_c^{NRHEG}(n)$). The RLDA correlation energies obtained by solution of (3.25) (using the RLDA for the complete v_{xc}^L) for a number of atoms are listed in Table 5.6 and compared with the usual quantum chemical correlation energy E_c^{RCI} ,

$$E_c^{RCI} = E_{tot} - E_{tot}^{RHF} - \Delta E^{QED}. \quad (5.10)$$

Here the RHF ground state energy E_{tot}^{RHF} is understood to include the transverse exchange energy contribution as well as the finite nuclear size correction and ΔE^{QED} represents all quantum electrodynamical corrections (when extracting E_{tot} from experimental data also the finite nuclear mass has to be taken into account [107]). Consequently E_c^{RCI} contains all relativistic correlation contributions. Unfortunately, except for two-electron systems, E_{tot}^{RHF} is not identical with the corresponding ROPM ground state energy so that the exact density functional E_c does not exactly agree with E_c^{RCI} but is somewhat larger in magnitude. This small difference is, however, irrelevant for the present purpose, so that one may use E_c^{RCI} as a reference standard¹⁹. The same holds for the nonrelativistic quantum chemical correlation energy,

$$E_c^{NRCI} = E_{tot}^{NR} - E_{tot}^{NRHF}, \quad (5.11)$$

with respect to the nonrelativistic E_c . Moreover, full CI results are only available for rather small atoms so that we resort to data of second order many-body perturbation theory (MBPT2) for E_c^{NRCI} and for E_c^{RCI} [108] in the case of the more interesting large atoms. On the level of accuracy required for the present purpose the differences between MBPT2 and full CI energies are not relevant.

Table 5.6 demonstrates once more the well known fact that the nonrelativistic LDA overestimates the exact atomic correlation energies by about a factor of 2. Here, however, not the accuracy of the complete functional (4.10) is of interest, but rather the relativistic corrections ΔE_c^L and E_c^T , as the correction scheme (4.10) could be combined with more accurate nonrelativistic $E_c[n]$ like GGAs. Table 5.6 shows that both ΔE_c^L and E_c^T are much smaller than their x-only counterparts. On the other hand, ΔE_c^L and E_c^T add up constructively so that the total correction $\Delta E_c^L + E_c^T$ is somewhat closer to $\Delta E_x^L + E_x^T$ than the individual components: For Hg one obtains $\Delta E_c^L + E_c^T = -0.49 \text{hartree}$ within MBPT2 compared with the exact $\Delta E_x^L + E_x^T$ of about 2.19hartree . Nevertheless, in absolute values the relativistic corrections to $E_c[n]$ are clearly less important than those to $E_x[n]$.

¹⁹ Note that the presently remaining numerical uncertainty in the available CI-correlation energies is much smaller than the error of the RLDA discussed here.

Table 5.6. Comparison of LDA [36], CI (estimated from nonrelativistic CI-calculations for the three innermost electrons and the experimental ionisation potentials of all other electrons [109]) and MBPT2 [108] correlation energies for neutral atoms: E_c^{NR} — nonrelativistic correlation energy, ΔE_c^L — relativistic contribution in the longitudinal correlation energy, E_c^T — transverse correlation energy (in the case of the MBPT2 only the dominating Breit contribution to E_c^T is given — all energies are in *hartrees*).

Atom	$-E_c^{NR}$		$-\Delta E_c^L$		$-E_c^T$		
	MBPT2	CI	LDA	MBPT2	LDA	MBPT2	LDA
He	37.14	42.04	111.47	0.00	0.00	0.04	0.00
Be		94.34	224.44		0.02		0.02
Ne	383.19	390.47	743.38	0.20	0.38	1.87	0.32
Mg		438.28	891.42		0.75		0.57
Ar	697.28	722.16	1429.64	0.84	2.60	7.92	1.89
Zn	1650.61		2665.20	10.51	10.97	26.43	7.92
Kr	1835.43		3282.95	11.39	19.61	41.07	13.10
Cd	2618.11		4570.56	35.86	44.79	82.32	28.58
Xe	2921.13		5200.19	37.57	64.73	108.75	39.27
Hg	5086.24		8355.68	203.23	200.87	282.74	113.08
Rn	5392.07		9026.90	195.36	257.00	352.60	138.43

Concerning the accuracy of $\Delta E_c^{L,RLDA}$ and $E_c^{T,RLDA}$ two features are immediately clear from Table 5.6: On the one hand, the MBPT2 energies do not increase with Z as smoothly as the corresponding RLDA results. On the other hand, while the LDA results for ΔE_c^L agree with the MBPT2 values at least for some atoms, the magnitude of E_c^T from the MBPT2 is not reproduced by the RLDA. It seems unlikely that the drastic deviation of the RLDA for E_c^T can be explained by the fact that in contrast to the RLDA in the case of the MBPT2 only the Breit limit of the full transverse interaction has been used, in particular in view of the similarity of $E_x^{T,Breit}$ and E_x^T shown in Table 5.5. Thus the overall relative error for ΔE_c^L and E_c^T in the RLDA is even larger than that for ΔE_x^L and E_x^T . Note, however, that the underestimation of E_c^T in the RLDA might be reduced by inclusion of the relativistic corrections of order e^4 which are neglected in the RPA.

The inappropriate scaling of the RLDA with Z , and thus also with β , becomes particularly obvious for fixed electron number. In Fig.5.5 the percentage deviations of the RLDA for ΔE_c^L and E_c^T are shown for the Ne isoelectronic series. The error for the correlation energy in the RLDA shows little tendency to approach zero with increasing Z , indicating that the relativistic correction factor Φ_c^{RPA} plotted in Fig.4.4 is inadequate for electronic structure calculations.

In summary, the RLDA addresses relativistic corrections to $E_c[n]$ on the same limited level of sophistication as the NRLDA does for the nonrelativistic correlation energy functional. Even more than in the case of exchange,

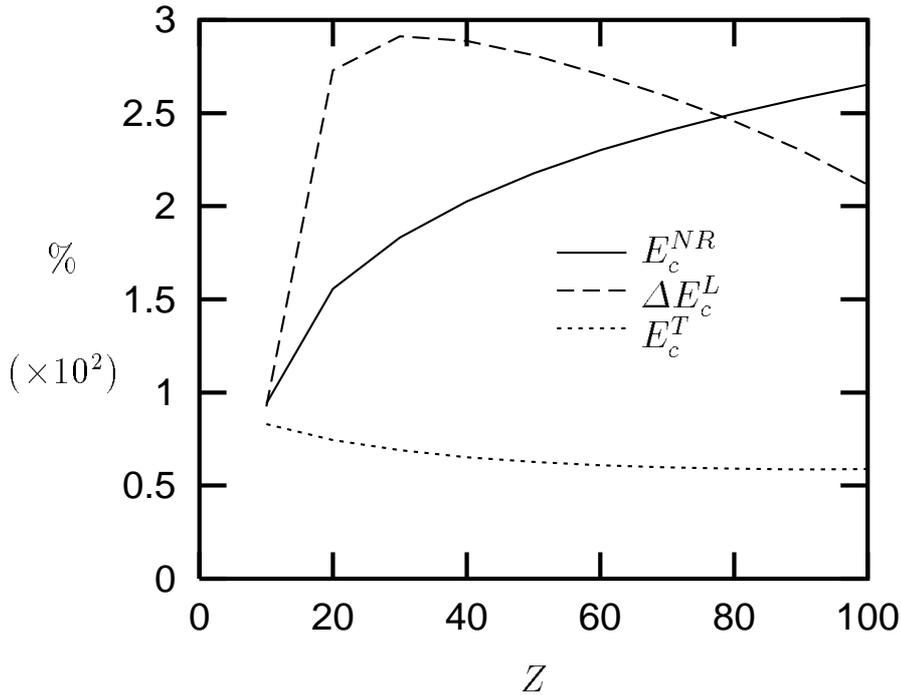


Fig. 5.5. Percentage deviation of the LDA for $E_c[n]$ from MBPT2 results [108] for the Ne isoelectronic series. For E_c^T the absolute value of the error has been plotted (note the scale).

nonlocal corrections seem to be required for a really satisfactory description of (relativistic) correlation effects in atoms.

6. Concluding Remarks

On the basis of the rather limited applications of RDFT the following comments can be offered.

The ROPM can be readily formulated and applied for the case of the longitudinal exchange in the no-pair approximation. It yields results for ground state and exchange energies as well as highest occupied eigenvalues which are very close to the corresponding RHF results. This demonstrates the possibility to approach the exchange contributions (including the necessary self interaction corrections) in terms of a local (i.e. multiplicative) rather than a nonlocal potential. The next goal is the inclusion of transverse exchange contributions in the ROPM scheme.

Concerning the RLDA it is found that the errors already present in the nonrelativistic case are enhanced in the relativistic regime: The error of the total longitudinal exchange energy, which is dominated by its nonrelativistic ingredients, is of the order of 10% in the small- Z regime and reduces to about 5% for heavier atoms. The relativistic corrections in the longitudinal

exchange energy are, however, underestimated in magnitude by about 20% and the transverse contribution to the exchange energy is overestimated by more than 50%. As both errors add up rather than cancel, the total relativistic correction to atomic exchange energies is rather poorly reproduced by the RLDA. This picture is confirmed by the local errors found for the longitudinal exchange potential. In order to improve the situation, it seems necessary to work towards a relativistic extension of the generalised gradient approximation, which proved to be quite successful in the nonrelativistic regime.

The relative success of the nonrelativistic LDA is to some extent due to a fortunate partial cancellation of errors between the exchange and the correlation contributions. As the importance of correlation effects decreases with increasing nuclear charge, this situation does not occur in the relativistic regime. For the present, the discussion of correlation effects was based on the RLDA form suggested by Eq.(4.10) which essentially contains a nonrelativistic functional in the LDA augmented by relativistic corrections within the RPA. The results obtained with this functional can not be considered to be satisfactory. It remains to be investigated whether the two corrective options offered, (i) use of a more accurate nonrelativistic correlation functional, and (ii) inclusion of all relativistic correlation contributions of the order e^4 besides the RPA, will improve this situation. The next possible step, the evaluation of relativistic gradient corrections for the case of the correlation energy, would certainly constitute an extensive task, even on the lowest possible level.

The investigation of the RWDA, be it in the simplest form on the basis of the x-only pair correlation function of the RHEG, demonstrated that the problems of the RLDA with the cancellation of the self interaction and with the (related) asymptotic form of the x-only potential are only corrected in part in this approximation. On the other hand, the performance of this RWDA is definitely superior with respect to the relativistic corrections (near the nucleus). Thus further improvement might be possible if a refined relativistic pair correlation function is used.

Quite generally, it must be stated that some additional effort is required to develop the RDFT towards the same level of sophistication that has been achieved in the nonrelativistic regime. In particular, all exchange-correlation functionals, which are available so far, are functionals of the density alone. An appropriate extension of the nonrelativistic spin density functional formalism on the basis of either the time reversal invariance or the assembly of current density contributions (which are e.g. accessible within the gradient expansion) is one of the tasks still to be undertaken.

In addition, there is interest to further extend the discussion to a variety of situations, that have recently gained much attention in the nonrelativistic case, as time-dependent systems [49], excited states [45] or finite temperature ensembles [110]. As an example of work along these lines we mention the

gradient expansion of the noninteracting, relativistic free energy [110], leading to a temperature dependent relativistic extended Thomas-Fermi model.

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Note added:

After this manuscript was completed, a contribution presenting an orbital dependent self interaction correction for the relativistic LDA xc-energy functional has been published [111].

A. Relevant Aspects of Vacuum QED

In the first Appendix we outline some basic features of vacuum QED (without external potential) in order to establish our notation (adjusted to allow a direct comparison with nonrelativistic DF results) and to provide details of the renormalisation procedure for Greens functions and ground state energies utilised in Sections 2.,3. and the Appendices B.,C..

We consider the Lagrangian specified by Eqs.(2.1-2.6) without external sources,

$$V_\mu(\mathbf{x}) = 0 . \tag{A.1}$$

Due to the fact that the Lagrangian incorporates the creation and destruction of field quanta, not even the time-development of a single particle is a simple matter. The time development can be expressed in terms of the electron (fermion) and photon propagators, which are defined as the vacuum expectation values of the time-ordered product of field operators. For the fermions one has

$$G_V(x, y) = -i \langle 0 | \mathbf{T} \hat{\psi}(x) \hat{\bar{\psi}}(y) | 0 \rangle , \tag{A.2}$$

and for the photons

$$D_V^{\mu\nu}(x, y) = -i\epsilon^2 \langle 0 | \mathbf{T} \hat{A}^\mu(x) \hat{A}^\nu(y) | 0 \rangle . \tag{A.3}$$

As a consequence of translational invariance both quantities are functions of the difference of the Minkowski coordinates only, so that their four-dimensional Fourier transform can be written as

$$G_V(x - y) = \int \frac{d^4 p}{(2\pi)^4} e^{-ip \cdot (x-y)} G_V(p) \tag{A.4}$$

$$D_V^{\mu\nu}(x - y) = \int \frac{d^4 q}{(2\pi)^4} e^{-iq \cdot (x-y)} D_V^{\mu\nu}(q) . \tag{A.5}$$

The standard approach to the calculation of the propagators (A.4,A.5) is perturbation theory with respect to the electron-electron coupling constant $\alpha = e^2/(\hbar c)$ on the basis of the interaction picture. Technically this results in an expansion of expectation values of interacting field operators in powers of expectation values of the free (or noninteracting) field operators $\hat{\psi}_0$ and \hat{A}_0^μ . The structure of this expansion can be summarised in a set of formal rules, the Feynman-rules. For instance for the electron propagator one obtains ²⁰

$$G_V(x-y) = -i \frac{\langle 0_0 | \mathbf{T} \hat{\psi}_0(x) \hat{\bar{\psi}}_0(y) \exp[-ie \int d^4z \hat{\bar{\psi}}_0(z) \hat{A}_0(z) \hat{\psi}_0(z)] | 0_0 \rangle}{\langle 0_0 | \mathbf{T} \exp[-ie \int d^4z \hat{\bar{\psi}}_0(z) \hat{A}_0(z) \hat{\psi}_0(z)] | 0_0 \rangle},$$

which allows an immediate expansion in powers of e . Each power introduces an additional integration $\int d^4z$ (called loop integration), while (using Wick's theorem) the corresponding integrands consist of three basic elements, i.e. the expectation values of the free field operators,

$$G_V^0(x-y) = -i \langle 0_0 | \mathbf{T} \hat{\psi}_0(x) \hat{\bar{\psi}}_0(y) | 0_0 \rangle \quad (\text{A.6})$$

$$D^{0,\mu\nu}(x-y) = -ie^2 \langle 0_0 | \mathbf{T} \hat{A}_0^\mu(x) \hat{A}_0^\nu(y) | 0_0 \rangle \quad (\text{A.7})$$

and their link, the vertex,

$$\gamma^\mu \delta^{(4)}(z_1 - z_3) \delta^{(4)}(z_2 - z_3),$$

where the z_i represent the coordinates of the three field operators linked at the vertex. For homogeneous systems this expansion is most easily performed in momentum space, leading to loop integrations over four momenta rather than space-time coordinates. In momentum space the free (or noninteracting) electron propagator G_V^0 , which represents the $e^2 \rightarrow 0$ limit of G_V , reads

$$G_V^0(p) = \frac{\not{p} + m}{p^2 - m^2 + i\epsilon}. \quad (\text{A.8})$$

The form of the free photon propagator $D_{\mu\nu}^0$ depends on the choice of gauge, that is the parameter λ in the Lagrangian (2.1). In Landau gauge, corresponding to the choice $\lambda = \infty$, one has

$$D_{\mu\nu}^0(q) = \left(g_{\mu\nu} - \frac{q_\mu q_\nu}{q^2} \right) D^0(q) \quad ; \quad D^0(q) = \frac{-4\pi e^2}{q^2 + i\epsilon}. \quad (\text{A.9})$$

The standard decomposition of $D_{\mu\nu}^0(x-y)$ into the nonretarded Coulomb (longitudinal) and the transverse contribution [29],

²⁰ The occurrence of the denominator expression leads, speaking in diagrammar, to the elimination of all unconnected diagrams, i.e. it reflects the proper normalisation of $G_V(x-y)$. $|0_0\rangle$ represents the free vacuum, to be distinguished from the vacuum $|0\rangle$ of the interacting theory.

$$D_{\mu\nu}^0(x-y) = D_{\mu\nu}^{0,L}(x-y) + D_{\mu\nu}^{0,T}(x-y) \quad (\text{A.10})$$

$$D_{\mu\nu}^{0,L}(x-y) = e^2 g_{0\mu} g_{0\nu} \frac{\delta(x^0 - y^0)}{|\mathbf{x} - \mathbf{y}|}, \quad (\text{A.11})$$

implies that the longitudinal part of $D_{\mu\nu}^0(q)$ is identical with the Coulomb interaction,

$$D_{\mu\nu}^{0,L}(q) = g_{0\mu} g_{0\nu} D_L^0(\mathbf{q}) \quad ; \quad D_L^0(\mathbf{q}) = \frac{4\pi e^2}{\mathbf{q}^2}. \quad (\text{A.12})$$

The third basic element of the perturbation expansion, the vertex, which describes the emission or absorption of a photon by a fermion (in lowest order), is given by γ_μ in our notation (as usual, four momentum conservation is automatically implied at the vertices). In diagrammar the free propagators and the simple vertex will be represented by

$$G_{V,\alpha\beta}^0(p) = \alpha \xrightarrow{p} \beta \quad (\text{A.13})$$

$$iD_{\mu\nu}^0(q) = \mu \overset{q}{\sim} \nu \quad (\text{A.14})$$

$$\gamma_{\alpha\beta}^\mu = \begin{array}{c} \mu \\ \swarrow \quad \searrow \\ \alpha \quad \beta \end{array} \begin{array}{c} p_1 - p_2 \\ p_1 \quad p_2 \end{array}, \quad (\text{A.15})$$

where α, β are the spinor indices.

In the subsequent discussion we shall need the irreducible 2- and 3-point functions²¹, i.e. the electron self energy $\Sigma_V(p)$, the vacuum polarisation $\Pi_{V,\mu\nu}(q)$ and the full vertex function $\Gamma_{V,\mu}(p_1, p_2)$, as knowledge of $\Sigma_V(p)$ and $\Pi_{V,\mu\nu}(q)$ determines the corresponding propagators $G_V(p)$ and $D_{V,\mu\nu}(q)$ completely and $\Gamma_{V,\mu}(p_1, p_2)$ represents the perturbative corrections to the free vertex γ_μ . The connection between these quantities is established by the Dyson equations (see e.g.[26])

$$G_V(p) = G_V^0(p) + G_V^0(p) \Sigma_V(p) G_V(p) \quad (\text{A.16})$$

$$D_{V,\mu\nu}(q) = D_{\mu\nu}^0(q) + D_{\mu\rho}^0(q) \Pi_V^{\rho\lambda}(q) D_{V,\lambda\nu}(q). \quad (\text{A.17})$$

The relations (A.16-A.17) separate the nontrivial higher order contributions in the perturbation expansions for $G_V(p)$ and $D_{V,\mu\nu}(q)$ from trivial multiples of lower order terms, thus isolating the essential information contained in higher orders. These relations become particularly simple if (A.16) is rewritten in terms of inverse propagators,

²¹ n -point functions are called irreducible if their diagrammatic expansions only consist of graphs which do not split into two pieces if one internal electron or photon line is cut.

$$G_V(p)^{-1} = G_V^0(p)^{-1} - \Sigma_V(p) = \not{p} - m - \Sigma_V(p) , \quad (\text{A.18})$$

and if the tensor structure of $\Pi_V^{\mu\nu}(q)$,

$$\Pi_V^{\mu\nu}(q) = \left(q^2 g^{\mu\nu} - q^\mu q^\nu \right) \omega_V(q^2) , \quad (\text{A.19})$$

which results from gauge invariance, is used in (A.17),

$$D_{V,\mu\nu}(q) = \left(g_{\mu\nu} - \frac{q_\mu q_\nu}{q^2} \right) \frac{-4\pi e^2}{q^2 [1 + 4\pi e^2 \omega_V(q^2)]} . \quad (\text{A.20})$$

Moreover, $\Sigma_V(p)$ and $\Gamma_{V,\mu}(p_1, p_2)$ satisfy the Ward-Takahashi identity (see e.g.[26])

$$(p_\mu - p'_\mu) \Gamma_V^\mu(p, p') = \Sigma_V(p') - \Sigma_V(p) , \quad (\text{A.21})$$

which also is a manifestation of gauge invariance.

One encounters ultraviolet (UV) divergent contributions to the electron and photon propagators as well as the vertex function already in the first order of the perturbation expansion. These UV-divergent first order contributions (1-loop contributions) correspond to the following diagrams for the irreducible 2- and 3-point functions:

The electron self energy,

$$\Sigma_V^{(1)}(p) = p - q \left[\text{diagram: a fermion line with a photon loop} \right] q , \quad (\text{A.22})$$

the vacuum polarisation,

$$-i\Pi_{V,\mu\nu}^{(0)}(q) = \text{diagram: a photon loop with fermion lines} , \quad (\text{A.23})$$

and the vertex function,

$$\Gamma_{V,\mu}^{(1)}(p_1, p_2) = \text{diagram: a fermion line with a photon loop at the vertex} . \quad (\text{A.24})$$

Transcription of the diagrammar into explicit equations using standard Feynman rules (within the notation chosen here) yields

$$\Sigma_V^{(1)}(p) = i \int \frac{d^4 q}{(2\pi)^4} D_{\mu\nu}^0(q) \gamma^\mu G_V^0(p-q) \gamma^\nu \quad (\text{A.25})$$

$$\Pi_{V,\mu\nu}^{(0)}(q) = -i \int \frac{d^4 p}{(2\pi)^4} \text{tr} \left[\gamma_\mu G_V^0(p) \gamma_\nu G_V^0(p-q) \right] , \quad (\text{A.26})$$

where the extra minus sign in (A.26) arises from the Feynman rule concerning closed fermion loops and the trace is to be taken in spinor space, as well as

$$\Gamma_{V,\mu}^{(1)}(p_1, p_2) = i \int \frac{d^4 k}{(2\pi)^4} D_{\rho\nu}^0(k) \gamma^\rho G_V^0(p_1 - k) \gamma_\mu G_V^0(p_2 - k) \gamma^\nu . \quad (\text{A.27})$$

If one evaluates the integrals over the loop momenta one finds that neither of the quantities is well-defined. One method to endow these quantities with a meaning is the counterterm technique, based e.g. on dimensional regularisation (see e.g.[112, 26]). In this method one first evaluates the integrals (A.25-A.27) not in (1,3)-dimensional Minkowski space but in a (1,d-1)-dimensional space. The results evaluated for integer dimension can then be analytically continued to noninteger d , allowing to consider the physically interesting limit $d \rightarrow 4$. Using the abbreviation $\Delta = (4 - d)/2$ one finds for the integrals²² (A.25-A.27),

$$\Sigma_V^{(1)}(p) = \frac{e^2}{16\pi^2} \Gamma(\Delta)(-\not{p} + 4m) + \Sigma_{V,finite}^{(1)}(p) \quad (\text{A.28})$$

$$\Pi_{V,\mu\nu}^{(0)}(q) = (q^2 g_{\mu\nu} - q_\mu q_\nu) \left(\frac{1}{12\pi^2} \Gamma(\Delta) + \omega_{V,finite}^{(0)}(q^2) \right) \quad (\text{A.29})$$

$$\Gamma_{V,\mu}^{(1)}(p_1, p_2) = \frac{e^2}{16\pi^2} \Gamma(\Delta) \gamma_\mu + \Gamma_{V,\mu,finite}^{(1)}(p_1, p_2) , \quad (\text{A.30})$$

where $\Gamma(\Delta)$ is Euler's Γ -function in which the UV-divergences of the loop-integrals are isolated,

$$\Gamma(\Delta) \xrightarrow{\Delta \rightarrow 0} \frac{1}{\Delta} + \dots ,$$

while inside the finite remainders the limit $d \rightarrow 4$ can be taken directly. These finite parts, which are not of immediate interest in the present context, correspond to rather lengthy expressions (for the static limit of $\omega_{V,finite}^{(0)}(q^2)$ see Eq.(B.38)). The general feature that emerges from dimensional regularisation is the isolation of the divergent contributions to the integrals in question: In all cases one finds a simple pole structure in the deviation of the space-time dimensionality from $d = 4$.²³ For the discussion of the next step, the actual renormalisation, one starts with the unrenormalised Lagrangian density, that is the Lagrangian of the form (2.1-2.4) with the (finite) physical mass m and charge e and physical (interacting) field operators

$$\mathcal{L}_{unren} = \mathcal{L}(\hat{\psi}, \hat{A}_\mu, m, e) . \quad (\text{A.31})$$

As the 2- and 3-point functions $\Sigma_V^{(1)}$, $\Pi_{V,\mu\nu}^{(0)}$ and $\Gamma_{V,\mu}^{(1)}$ calculated on the basis of this Lagrangian are divergent, it is necessary to add a so-called counterterm Lagrangian

²² For brevity we suppress all problems related to infrared divergencies in the following.

²³ It is perhaps interesting to note that the divergent contributions to $\Sigma_V^{(1)}$ and $\Gamma_{V,\mu}^{(1)}$ satisfy the identity (A.21).

$$\mathcal{L}_{CT} = \mathcal{L}(\hat{\psi}, \hat{A}_\mu, A, B, \dots) \quad (\text{A.32})$$

in order to eliminate the divergencies. The crucial observation for both the physical interpretation as well as the technical success of this *at first glance* somewhat artificial step is the fact that the divergent contributions to the three relevant functions, Eqs.(A.28-A.30), essentially repeat the forms of the corresponding free propagators and the free vertex: The divergent part of $\Sigma_V^{(1)}$ is just proportional to \not{p} and m , but not e.g. to p^2 , the divergent part of $\Pi_{V,\mu\nu}^{(0)}$ repeats the tensor structure of $D_{\mu\nu}^0$, Eq.(A.9), and the divergent part of $\Gamma_{V,\mu}^{(1)}$ is proportional to the free vertex γ_μ (but not dependent on p_μ). Thus the contributions (counterterms) to be generated by (A.32) have the form of free propagators and the free vertex with modified physical constants m and e as well as modified normalisation. As a consequence the operator structure of the counterterm Lagrangian is identical to that of the initial Lagrangian (A.31), so that the sum $\mathcal{L}_{unren} + \mathcal{L}_{CT}$ can be combined in the form

$$\mathcal{L}_R = \mathcal{L}_{unren} + \mathcal{L}_{CT} = \mathcal{L}_{unren}(\sqrt{Z_2}\hat{\psi}, \sqrt{Z_3}\hat{A}_\mu, m - \delta m, \frac{Z_1 e}{Z_2 \sqrt{Z_3}}) \quad (\text{A.33})$$

Thus the renormalisation procedure simply amounts to a redefinition of the physical constants and operators in the initial Lagrangian, leaving the physical implications of this Lagrangian unmodified.

This procedure is readily demonstrated (on the 1-loop level) for the case of the "mass renormalisation". Here one has with (A.18) and (A.28)

$$G_V^{(1)}(p)^{-1} = \not{p} \left(1 + \frac{e^2}{16\pi^2} \Gamma(\Delta) \right) - m \left(1 + \frac{e^2}{4\pi^2} \Gamma(\Delta) \right) - \Sigma_{V,finite}^{(1)}(p) \quad (\text{A.34})$$

In order to compensate the divergent terms (in the limit $d \rightarrow 4$), one adds to the electron part of the unrenormalised Lagrangian the counterterm Lagrangian

$$\mathcal{L}_{e,CT} = \hat{\bar{\psi}}(x) (iA\not{\partial} - B) \hat{\psi}(x) \quad (\text{A.35})$$

so that the renormalised electron Lagrangian reads

$$\mathcal{L}_{e,R} = \hat{\bar{\psi}}(x) (i(1+A)\not{\partial} - (m+B)) \hat{\psi}(x) \quad (\text{A.36})$$

Evaluating the electron propagator on the one loop level as before (using the same \mathcal{L}_{int}) one finds to first order

$$G_{V,R}^{(1)}(p)^{-1} = \not{p} \left(1 + A + \frac{e^2}{16\pi^2} \Gamma(\Delta) \right) - m \left(1 + \frac{B}{m} + \frac{e^2}{4\pi^2} \Gamma(\Delta) \right) - \Sigma_{V,finite}^{(1)}(p), \quad (\text{A.37})$$

so that the choice

$$A = -\frac{e^2}{16\pi^2} \Gamma(\Delta) \quad B = -\frac{e^2 m}{4\pi^2} \Gamma(\Delta) \quad (\text{A.38})$$

$$\mathcal{L}_{e,R} = \widehat{\bar{\psi}}_b(x) (i\not{\partial} - m_b) \widehat{\psi}_b(x) \quad , \quad (\text{A.44})$$

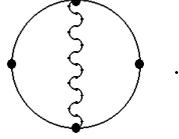
i.e. the counterterms required for keeping $\Sigma_{V,R}^{(1)}$ finite have been completely absorbed in a redefinition (or renormalisation) of the ingredients of the free electron part of \mathcal{L} . In terms of Z_2 and δm the resulting renormalised self energy then reads quite generally

$$\Sigma_{V,R}(p) = Z_2 \left[\Sigma_V(p) - \delta m \right] + (1 - Z_2)(\not{p} - m) \quad , \quad (\text{A.45})$$

so that the first order counterterm is given by

$$\begin{aligned} \Delta\Sigma_V^{(1)}(p) &= -\delta m^{(1)} + (1 - Z_2^{(1)})(\not{p} - m) \\ &= \frac{e^2}{16\pi^2} \Gamma\left(\frac{4-d}{2}\right) \not{p} - \frac{e^2}{4\pi^2} \Gamma\left(\frac{4-d}{2}\right) m \quad . \end{aligned} \quad (\text{A.46})$$

An equivalent procedure can be carried through for $\Pi_{V,\mu\nu}^{(0)}$ addressing \mathcal{L}_γ as well as $\Gamma_{V,\mu}^{(1)}$ addressing \mathcal{L}_{int} . The argument can be extended to any order, after discussion of overlapping divergencies, which occur for instance in the diagram



For the subsequent discussion we also note the normalisation condition for the vacuum polarisation kernel $\omega_{V,R}(q^2)$: In order to obtain the physical charge e for real electrons, i.e. to reproduce the Coulomb interaction for well separated electrons, $\omega_{V,R}(q^2)$ must vanish for vanishing momentum,

$$\omega_{V,R}(q^2 = 0) = 0 \quad , \quad (\text{A.47})$$

which is immediately obvious from the Dyson equation (A.20) for the full photon propagator. Consistent with (A.29) the counterterm for $\Pi_{V,\mu\nu}^{(0)}(q)$ reads

$$\Delta\Pi_{V,\mu\nu}^{(0)}(q) = -(q^2 g_{\mu\nu} - q_\mu q_\nu) \frac{1}{12\pi^2} \Gamma\left(\frac{4-d}{2}\right) \quad . \quad (\text{A.48})$$

The final form of the fully renormalised Lagrangian of QED is

$$\begin{aligned} \mathcal{L}_R &= \frac{1}{4} \left\{ \left[\widehat{\bar{\psi}}_b(x), \left(i\vec{\not{\partial}} - m_b - e_b \not{V}_b(\mathbf{x}) - e_b \hat{A}_b(x) \right) \widehat{\psi}_b(x) \right] \right. \\ &\quad \left. + \left[\widehat{\bar{\psi}}_b(x), \left(-i\vec{\not{\partial}} - m_b - e_b \not{V}_b(\mathbf{x}) - e_b \hat{A}_b(x) \right), \widehat{\psi}_b(x) \right] \right\} \\ &\quad - \frac{1}{16\pi} \hat{F}_{b,\mu\nu}(x) \hat{F}_b^{\mu\nu}(x) - \frac{\lambda}{8\pi} \left(\partial_\nu \hat{A}_b^\nu(x) \right)^2 \end{aligned} \quad (\text{A.49})$$

$$\begin{aligned}
 &= \frac{Z_2}{4} \left\{ \left[\hat{\psi}(x), \left(i\vec{\phi} - m + \delta m - e\Psi(\mathbf{x}) - e\hat{A}(x) \right) \hat{\psi}(x) \right] \right. \\
 &\quad \left. + \left[\hat{\bar{\psi}}(x) \left(-i\vec{\phi} - m + \delta m - e\Psi(\mathbf{x}) - e\hat{A}(x) \right), \hat{\psi}(x) \right] \right\} \\
 &\quad - \frac{Z_3}{16\pi} \hat{F}_{\mu\nu}(x) \hat{F}^{\mu\nu}(x) - \frac{Z_3\lambda}{8\pi} \left(\partial_\nu \hat{A}^\nu(x) \right)^2,
 \end{aligned}$$

where we have included the static external potential in order to indicate that it has to be renormalised in the same spirit as the quantised photon field. The physical fields and constants are related to the bare quantities by

$$\hat{\psi}_b(x) = \sqrt{Z_2} \hat{\psi}(x) \quad (\text{A.50})$$

$$\hat{A}_b^\nu(x) = \sqrt{Z_3} \hat{A}^\nu(x) \quad (\text{A.51})$$

$$V_b^\nu(\mathbf{x}) = \sqrt{Z_3} V^\nu(\mathbf{x}) \quad (\text{A.52})$$

$$e_b = \frac{Z_1}{Z_2 \sqrt{Z_3}} e \quad (\text{A.53})$$

$$m_b = m - \delta m \quad (\text{A.54})$$

The renormalisation constants Z_1 , Z_2 , Z_3 and δm have to be understood as functions of the finite physical charge e and mass m of the electrons which can be constructed order by order in the perturbation series. It is important to notice that these constants are uniquely determined by vacuum QED without any external potential. They do not depend on the specific external potential present. If one bases the perturbation expansion on the Lagrangian (A.49) all Greens and n -point functions of the theory (defined in terms of the physical fields $\hat{\psi}$ and \hat{A}^μ) are finite.

B. Relativistic Homogeneous Electron Gas

In this Appendix we summarise some properties of the relativistic homogeneous electron gas (RHEG) in order to illustrate the renormalisation of ground state energies (indicated in Section 2.) and to provide the details for the RLDA and the relativistic gradient expansion (RGE), which are discussed in Section 4. and Appendix D., respectively. For simplicity we restrict the discussion to the unpolarised RHEG.

We start by noting the basic difference between the perturbative approaches to the RHEG and the QED vacuum (discussed in Appendix A.). As a consequence of the difference between the ground state $|\Phi_0\rangle$ of the RHEG and the homogeneous vacuum $|0\rangle$ the fermion propagator

$$G(x, y) = -i \langle \Phi_0 | \mathbf{T} \hat{\psi}(x) \hat{\bar{\psi}}(y) | \Phi_0 \rangle, \quad (\text{B.1})$$

already differs from G_V on the noninteracting level. In our notation the noninteracting fermion propagator of the RHEG is given by

$$G^0(p) = G_V^0(p) + G_D^0(p) = G_-(p) + G_+(p) \quad (\text{B.2})$$

$$G_D^0(p) = 2\pi i \delta(p^0 - E_p) \frac{\not{p} + m}{2E_p} \Theta(k_F - |\mathbf{p}|) \quad (\text{B.3})$$

$$G_-(p) = \frac{\not{p}_- + m}{2E_p} \frac{-1}{p^0 + E_p - i\epsilon} \quad (\text{B.4})$$

$$G_+(p) = \frac{\not{p}_+ + m}{2E_p} \left[\frac{\Theta(|\mathbf{p}| - k_F)}{p^0 - E_p + i\epsilon} + \frac{\Theta(k_F - |\mathbf{p}|)}{p^0 - E_p - i\epsilon} \right], \quad (\text{B.5})$$

where $E_p = \sqrt{\mathbf{p}^2 + m^2}$, $p_\pm^\mu = (\pm E_p, p^i)$ and the Fermi momentum k_F is related to the electron density n_0 of the RHEG as usual, $n_0 = k_F^3/(3\pi^2)$. Here two alternative forms have been listed, the first one emphasising the relation between $G^0(p)$ and the vacuum propagator $G_V^0(p)$, Eq.(A.8), the second one visualising its decomposition into the electron (G_+) and positron (G_-) contributions. Note that due to charge conservation the density of the RHEG is not changed by switching on the electron-electron interaction, so that n_0 also represents the density of the interacting RHEG and $n_0 = k_F^3/(3\pi^2)$ then relates the interacting density to the noninteracting k_F . Diagrammatically the full $G^0(p)$, Eq.(B.2), will be represented by

$$G^0(p) = \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \quad (\text{B.6})$$

in the following.

While the other two basic elements of perturbation theory, the free photon propagator (A.9) and the simple vertex, remain unchanged, it seems worth pointing out that the full photon propagator

$$D_{\mu\nu}(x, y) = -ie^2 \langle \Phi_0 | \mathbf{T} \hat{A}_\mu(x) \hat{A}_\nu(y) | \Phi_0 \rangle, \quad (\text{B.7})$$

and the full vertex function do not: In the case of the RHEG not only virtual electron-positron pairs screen the bare interaction but also virtual electron-hole pairs.

B.1 Response Functions

Most information concerning the RHEG required in the present context is contained in the response functions of the RHEG. In our notation the time-ordered current response functions (n -point functions) are defined as

$$\chi_{\mu_1 \dots \mu_n}^{(n)}(x_1, \dots, x_n) = (-i)^{n-1} \langle \Phi_0 | \mathbf{T} \hat{j}_{\mu_1}(x_1) \dots \hat{j}_{\mu_n}(x_n) | \Phi_0 \rangle, \quad (\text{B.8})$$

where the current deviation operator \hat{j}_μ is given by

$$\hat{j}_\mu(t, \mathbf{r}) = \hat{j}_\mu(t, \mathbf{r}) - \langle \Phi_0 | \hat{j}_\mu(t, \mathbf{r}) | \Phi_0 \rangle = \hat{j}_\mu(t, \mathbf{r}) - j_\mu(\mathbf{r}). \quad (\text{B.9})$$

For the time-independent systems of interest here a partial Fourier transformation of $\chi_{\mu_1 \dots \mu_n}^{(n)}$ is advantageous,

$$\begin{aligned} \chi_{\mu_1 \dots \mu_n}^{(n)}(t_1, \mathbf{r}_1; \dots t_n, \mathbf{r}_n) &= \int \frac{d\omega_1}{2\pi} \dots \int \frac{d\omega_n}{2\pi} e^{-i\omega_1 t_1 - \dots - i\omega_n t_n} \\ &\times 2\pi \delta(\omega_1 + \dots + \omega_n) \chi_{\mu_1 \dots \mu_n}^{(n)}(\omega_1, \mathbf{r}_1; \dots \omega_n, \mathbf{r}_n). \end{aligned} \quad (\text{B.10})$$

The static response functions utilised in Appendix C. are then obtained by taking the zero-frequency limit,

$$\chi_{\mu_1 \dots \mu_n}^{(n)}(\mathbf{r}_1, \dots \mathbf{r}_n) \equiv \chi_{\mu_1 \dots \mu_n}^{(n)}(\omega_1 = 0, \mathbf{r}_1; \dots \omega_n = 0, \mathbf{r}_n). \quad (\text{B.11})$$

For the case of the RHEG further Fourier transformation is useful,

$$\begin{aligned} \chi_{\mu_1 \dots \mu_n}^{(n)}(q_1^0, \mathbf{r}_1; \dots q_n^0, \mathbf{r}_n) &= \int \frac{d^3 q_1}{(2\pi)^3} \dots \int \frac{d^3 q_n}{(2\pi)^3} e^{i\mathbf{r}_1 \cdot \mathbf{q}_1 + \dots + i\mathbf{r}_n \cdot \mathbf{q}_n} \\ &\times (2\pi)^3 \delta^{(3)}(\mathbf{q}_1 + \dots + \mathbf{q}_n) \chi_{\mu_1 \dots \mu_n}^{(n)}(q_1, \dots q_n). \end{aligned} \quad (\text{B.12})$$

Gauge invariance then implies the transversality of the $\chi_{\mu_1 \dots \mu_n}^{(n)}$ with respect to all arguments [113],

$$q_i^{\mu_i} \chi_{\mu_1 \dots \mu_i \dots \mu_n}^{(n)}(q_1, \dots q_i, \dots q_n) = 0. \quad (\text{B.13})$$

In the following the connected contributions of the $\chi^{(n)}$, for which all external vertices are in some way linked to each other, will be denoted by $\chi_c^{(n)}$, while the linear response function of the RHEG will be abbreviated by $\chi_{\mu\nu}(q)$ for brevity.

As a consequence of (B.13) and the Dyson equation for $\chi^{\mu\nu}(q)$,

$$\chi^{\mu\nu}(q) = \Pi^{\mu\nu}(q) + \Pi^{\mu\rho}(q) D_{\rho\lambda}^0(q) \chi^{\lambda\nu}(q). \quad (\text{B.14})$$

the irreducible 2-point function $\Pi^{\mu\nu}(q)$ also satisfies the transversality relation,

$$q_\mu \Pi^{\mu\nu}(q) = 0, \quad (\text{B.15})$$

which essentially determines its tensor structure. Introducing the (4×4) polarisation tensors

$$P_L^{\mu\nu}(q) = \frac{-1}{\mathbf{q}^2 q^2} \begin{pmatrix} (\mathbf{q}^2)^2 & \mathbf{q}^2 q^0 q^j \\ \mathbf{q}^2 q^0 q^i & (q^0)^2 q^i q^j \end{pmatrix} \quad (\text{B.16})$$

$$P_T^{\mu\nu}(q) = \frac{1}{\mathbf{q}^2} \begin{pmatrix} 0 & 0 \\ 0 & \mathbf{q}^2 g^{ij} + q^i q^j \end{pmatrix}, \quad (\text{B.17})$$

$(g^{ij} = -\delta_{ij})$ $\Pi^{\mu\nu}(q)$ can be written as

$$\Pi^{\mu\nu}(q) = P_L^{\mu\nu}(q) \Pi_L(q) - P_T^{\mu\nu}(q) \Pi_T(q). \quad (\text{B.18})$$

For convenience, we note some useful properties of $P_{L/T}^{\mu\nu}(q)$,

$$P_{L,\mu}{}^\nu(q)P_{L,\nu}{}^\lambda(q) = P_{L,\mu}{}^\lambda(q) \quad (\text{B.19})$$

$$P_{T,\mu}{}^\nu(q)P_{T,\nu}{}^\lambda(q) = P_{T,\mu}{}^\lambda(q) \quad (\text{B.20})$$

$$P_{L,\mu}{}^\nu(q)P_{T,\nu}{}^\lambda(q) = 0 \quad (\text{B.21})$$

$$P_{L,\mu}{}^0(q)P_{L,0}{}^\lambda(q) = -\frac{\mathbf{q}^2}{q^2}P_{L,\mu}{}^\lambda(q) \quad (\text{B.22})$$

$$P_L^{\mu\nu}(q) + P_T^{\mu\nu}(q) = g^{\mu\nu} - \frac{q^\mu q^\nu}{q^2} \quad (\text{B.23})$$

$$P_{L,\mu}{}^\mu(q) = 1 \quad (\text{B.24})$$

$$P_{T,\mu}{}^\mu(q) = 2. \quad (\text{B.25})$$

Decomposing $\Pi^{\mu\nu}(q)$ into an electron gas (D) and the vacuum (V) component,

$$\Pi^{\mu\nu}(q) = \Pi_D^{\mu\nu}(q) + \Pi_V^{\mu\nu}(q) \quad (\text{B.26})$$

$$\Pi_L(q) = \Pi_{L,D}(q) + \Pi_V(q) \quad (\text{B.27})$$

$$\Pi_T(q) = \Pi_{T,D}(q) - \Pi_V(q), \quad (\text{B.28})$$

the vacuum contribution can be recast in the form (A.19), with the polarisation function $\Pi_V(q)$ given by

$$\Pi_V(q) = q^2\omega_V(q). \quad (\text{B.29})$$

Using the polarisation tensors (B.16,B.17), the free photon propagator (A.9) and the longitudinal and transverse polarisation functions $\Pi_{L/T}(q)$ the Dyson equation for $\chi^{\mu\nu}(q)$ reads

$$\chi^{\mu\nu}(q) = \frac{\Pi_L(q)}{1 - D^0(q)\Pi_L(q)}P_L^{\mu\nu}(q) - \frac{\Pi_T(q)}{1 + D^0(q)\Pi_T(q)}P_T^{\mu\nu}(q). \quad (\text{B.30})$$

The full photon propagator $D^{\mu\nu}(q)$ can be directly obtained from the Dyson equation (A.17) (which also holds for the RHEG) by insertion of (B.18). For a discussion of the renormalisation of $D^{\mu\nu}(q)$ it is instructive to rewrite the form corresponding to (B.30) by introducing the full vacuum photon propagator,

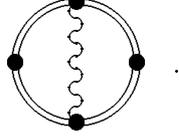
$$D_V(q) = \frac{D^0(q)}{1 - D^0(q)\Pi_V(q)}, \quad (\text{B.31})$$

which allows to 'decouple' the screening effects entirely due to the vacuum from those originating from the actual electron gas,

$$D^{\mu\nu}(q) = \frac{D_V(q)}{1 - D_V(q)\Pi_{L,D}(q)}P_L^{\mu\nu}(q) + \frac{D_V(q)}{1 + D_V(q)\Pi_{T,D}(q)}P_T^{\mu\nu}(q). \quad (\text{B.32})$$

At first glance this form seems to suggest that $D^{\mu\nu}(q)$ is UV-finite as soon as $D_V(q)$ has been renormalised, which amounts to replacing $D_V(q)$ by $D_{V,R}(q)$.

However, $\Pi_{L/T,D}(q)$ also contains UV-divergent subgraphs. The following 2-loop contribution may illustrate this point,



Replacing G^0 by $G_V^0 + G_D^0$ one recognises that besides the obvious pure vacuum loop absorbed in D_V also mixtures between the first order vacuum vertex correction loop (A.24) and G_D^0 -type propagators occur. The counterterms required to keep such subgraphs finite are, however, completely determined by vacuum QED: Similar to the renormalisation of overlapping divergencies each vacuum subgraph in a (larger) non-vacuum diagram has to be supplemented individually by the corresponding counterterm (this also holds for multi-loop vacuum subgraphs). The same procedure applies to $\chi^{\mu\nu}(q)$.

We also indicate the purely longitudinal limit of $\chi^{\mu\nu}(q)$,

$$\chi_L^{\mu\nu}(q) = \frac{\Pi_{LL}(q)}{1 - D^0(q)\Pi_{LL}(q)} P_L^{\mu\nu}(q) - \Pi_{TL}(q) P_T^{\mu\nu}(q), \quad (\text{B.33})$$

where $\Pi_{LL/TL}(q)$ is obtained from $\Pi_{L/T}(q)$ by replacing all internal photon propagators by $D_{\mu\nu}^{0,L}(q)$ (note that in the denominator $D^0(q)$ appears rather than $D_L^0(q)$ due to the properties of $P_L^{\mu\nu}(q)$, i.e. Eq.(B.22)).

For the discussion of inhomogeneity corrections to the RLDA one also needs the inverse response function $\chi_{\mu\nu}^{-1}(q)$, at least in the static limit,

$$\chi^{-1,\mu\nu}(q^0 = 0, \mathbf{q}) = -g^{\mu\nu} D_L^0(\mathbf{q}) + \Pi^{-1,\mu\nu}(q^0 = 0, \mathbf{q}) \quad (\text{B.34})$$

$$\Pi^{-1,\mu\nu}(q^0 = 0, \mathbf{q}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ \frac{1}{\Pi_L(0, \mathbf{q})} & 0 & 0 & 0 \\ 0 & \left(g^{ij} + \frac{q^i q^j}{\mathbf{q}^2}\right) & -1 & 0 \\ 0 & 0 & \frac{-1}{\Pi_T(0, \mathbf{q})} & 0 \end{pmatrix}. \quad (\text{B.35})$$

As far as explicit approximations for the polarisation functions $\Pi_{L/T}(q)$ are concerned only very little is known, even in the static limit. The complete frequency dependence is available for the noninteracting limit $\Pi_{L/T}^{(0)}(q)$, i.e. the relativistic generalisation of the Lindhard function [95, 114]. In addition to its vacuum part (A.26) one has

$$\begin{aligned} \Pi_{D,\mu\nu}^{(0)}(q) &= -i \int \frac{d^4 p}{(2\pi)^4} \text{tr} \left[\gamma_\mu G_D^0(p) \gamma_\nu G_D^0(p-q) \right] \\ &\quad -i \int \frac{d^4 p}{(2\pi)^4} \text{tr} \left[\gamma_\mu G_V^0(p) \gamma_\nu G_D^0(p-q) \right] \\ &\quad -i \int \frac{d^4 p}{(2\pi)^4} \text{tr} \left[\gamma_\mu G_D^0(p) \gamma_\nu G_V^0(p-q) \right] \end{aligned}$$

$$\neq -i \int \frac{d^4 p}{(2\pi)^4} \text{tr} \left[\gamma_\mu G_+^0(p) \gamma_\nu G_+^0(p-q) \right],$$

where it has been emphasised that the no-sea approximation is not just obtained by completely neglecting the 'positron propagator' $G_-(p)$ in the perturbation expansion (which would constitute the no-pair approximation for $\Pi_{L/T}^{(0)}$). Rather the no-sea approximation for any given diagram contributing to $\Pi_{\mu\nu}$ is defined by neglecting all those contributions to each fermion loop inside the diagram which do not vanish in the limit $k_F \rightarrow 0$. The static limit of $\Pi_{D,\mu\nu}^{(0)}$ and its small- \mathbf{q}^2 expansion are given by ($Q = |\mathbf{q}|/(2k_F)$),

$$\Pi_{L,D}^{(0)}(0, \mathbf{q}) \quad (\text{B.36})$$

$$\begin{aligned} &= -\frac{mk_F}{2\pi^2} \left\{ \frac{4}{3}\eta - \frac{4}{3}\beta Q^2 \text{arsinh}(\beta) + \frac{1}{3} \frac{\eta}{\beta^2 Q} \left(\eta^2 - 3\beta^2 Q^2 \right) \ln \left| \frac{1+Q}{1-Q} \right| \right. \\ &\quad \left. - \frac{1}{3} \frac{(1-2\beta^2 Q^2)(1+\beta^2 Q^2)^{1/2}}{\beta^2 Q} \ln \left| \frac{(1+\beta^2 Q^2)^{1/2} + \eta Q}{(1+\beta^2 Q^2)^{1/2} - \eta Q} \right| \right\} \\ &= -\frac{mk_F \eta}{\pi^2} \left\{ 1 - \frac{1}{3} \left[1 + 2\frac{\beta}{\eta} \text{arsinh}(\beta) \right] Q^2 - \frac{1}{15} [1 - 4\beta^2] Q^4 + \dots \right\} \end{aligned}$$

$$\Pi_{T,D}^{(0)}(0, \mathbf{q}) = -\Pi_{L,D}^{(0)}(0, \mathbf{q}) - \frac{mk_F \eta}{2\pi^2} \left\{ 1 + \frac{1-Q^2}{2Q} \ln \left| \frac{1+Q}{1-Q} \right| \right\} \quad (\text{B.37})$$

$$= \frac{mk_F \eta}{\pi^2} \left\{ -\frac{2}{3} \frac{\beta}{\eta} \text{arsinh}(\beta) Q^2 + \frac{4}{15} \beta^2 Q^4 + \dots \right\}$$

$$\Pi_{V,R}^{(0)}(0, \mathbf{q}) = \frac{\mathbf{q}^2}{12\pi^2} \left\{ \frac{1}{3} + \left(\frac{1-2\beta^2 Q^2}{\beta^2 Q^2} \right) \left[1 - \frac{(1+\beta^2 Q^2)^{1/2}}{2\beta Q} \right. \right. \quad (\text{B.38})$$

$$\left. \times \ln \left| \frac{(1+\beta^2 Q^2)^{1/2} + \beta Q}{(1+\beta^2 Q^2)^{1/2} - \beta Q} \right| \right\}$$

$$= \frac{1}{60\pi^2} \frac{\mathbf{q}^4}{m^2} + \dots,$$

where

$$\beta = \frac{(3\pi^2 n_0)^{\frac{1}{3}}}{m} \quad ; \quad \eta = (1 + \beta^2)^{\frac{1}{2}} \quad . \quad (\text{B.39})$$

Note that quite generally one has

$$\lim_{q^2 \rightarrow 0} \frac{\Pi_{V,R}(0, \mathbf{q})}{\mathbf{q}^2} = 0 \quad (\text{B.40})$$

due to the on-shell normalisation condition for $\omega_{V,R}$, Eq.(A.47). Beyond the noninteracting limit only the vacuum part of the first order (2-loop) contribution to the polarisation function [115, 116] has been evaluated. Moreover,

the screening length $\Pi_{L,D}(\mathbf{0}, 0)$ is related to the energy density via the compressibility sum rule [117],

$$\frac{d^2}{dn_0^2} \left[t_s(n_0) + e_{xc}(n_0) \right] = -\frac{1}{\Pi_{L,D}(0, \mathbf{0})} ,$$

so that the long wavelength limit of higher orders of $\Pi_{L,D}$ can be obtained from the associated contributions to $e_{xc}(n_0)$. Finally, in the context of the quark-gluon gas the high temperature limits of certain classes of higher order diagrams have also been examined (see e.g.[118]). These results are, however, only of limited value in the present context aiming at $T = 0$ and $m \neq 0$.

B.2 Ground State Energy

The ground state energy of the RHEG constitutes the basis for the RLDA and also provides an instructive example for the renormalisation procedure described in Section 2. and Appendix A.. We start by emphasising that the ground state energy is defined with respect to the vacuum energy as [96, 113]

$$E_{tot}^{RHEG} = \langle \Phi_0 | \hat{H}^{RHEG} | \Phi_0 \rangle - \langle 0 | \hat{H}^{RHEG} | 0 \rangle + \Delta E_{tot}^{RHEG} , \quad (\text{B.41})$$

where ΔE_{tot}^{RHEG} represents the additional counterterms beyond the energy of the homogeneous vacuum, $\langle 0 | \hat{H}^{RHEG} | 0 \rangle$, which are required to keep E_{tot}^{RHEG} UV-finite. Moreover, in the case of the RHEG one deals with the energy density corresponding to (B.41), rather than the energy itself.

The kinetic energy density of the noninteracting RHEG can be evaluated without addressing the UV-renormalisation procedure [12],

$$\begin{aligned} t_s(n_0) &= \langle \Phi_0 | \left[\hat{\bar{\psi}}(x), \left(-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + (1 - \gamma^0)m \right) \hat{\psi}(x) \right] | \Phi_0 \rangle \\ &\quad - \langle 0 | \left[\hat{\bar{\psi}}(x), \left(-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + (1 - \gamma^0)m \right) \hat{\psi}(x) \right] | 0 \rangle \\ &= i \lim_{y \rightarrow x} \text{tr} \left[\left(-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + (1 - \gamma^0)m \right) G_D^0(x - y) \right] \\ &= t_s^{NRHEG}(n_0) \Phi_{s,0}(\beta) \end{aligned} \quad (\text{B.42})$$

$$t_s^{NRHEG}(n_0) = \frac{1}{10\pi^2 m} k_F^5 \quad (\text{B.43})$$

$$\Phi_{s,0}(\beta) = \frac{10}{\beta^5} \left[\frac{1}{8} \left(\beta\eta^3 + \beta^3\eta - \text{arsinh}(\beta) \right) - \frac{1}{3}\beta^3 \right] , \quad (\text{B.44})$$

where the electron rest mass has been subtracted. Taking into account the homogeneous positive charge background the (direct) Hartree energy of the RHEG vanishes. The exchange-correlation energy can be written in terms of a coupling constant integral over the current-current response function [93, 98],

$$e_{xc}(n_0) = \frac{i}{2} \int_0^1 d\lambda \int \frac{d^4q}{(2\pi)^4} D_{\mu\nu}^0(q) \left[\chi_\lambda^{\mu\nu}(q) - \chi_{V,\lambda}^{\mu\nu}(q) \right] + \Delta E_{xc}^{RHEG}, \quad (\text{B.45})$$

where $\chi_\lambda^{\mu\nu}(q)$ is given by (B.30) with the electron-electron coupling strength e^2 replaced by λe^2 , $\chi_{V,\lambda}^{\mu\nu}(q)$ represents its vacuum limit and ΔE_{xc}^{RHEG} is identical with the total counterterm ΔE_{tot}^{RHEG} .

The first order term (in e^2) in (B.45), i.e. the exchange energy of the RHEG (according to Eq.(3.32)), is the most simple energy contribution for which the UV-renormalisation is nontrivial. The basic problem associated with the renormalisation of energies (rather than Greens functions) is that energy contributions can not be rewritten entirely in terms of renormalised n -point functions: At least one overall loop integration remains to be treated separately (as e.g. the q -integration in (B.45)), even if one takes into account the subtraction of the pure vacuum energy. As an additional complication, this outermost loop integration often leads to overlapping divergencies. In fact, visualising the exchange energy graphically

$$-2ie_x(n_0) = \text{Diagram 1} - \text{Diagram 2} \quad (\text{B.46})$$

one realises that three divergent 1-loop subgraphs contribute to the (left) electron gas loop,

$$-i\Pi_{\mu\nu}^{(0)} = \text{Diagram 3} \quad \Sigma^{(1)} = \text{Diagram 4} = \text{Diagram 5} \quad (\text{B.47})$$

While the UV-divergence of the $\Pi_{\mu\nu}^{(0)}$ -subgraph is eliminated by the subtraction of the vacuum exchange energy, the two (identical) self energy subgraphs require additional counterterms. As one is facing overlapping divergencies in (B.46) each divergent subgraph has to be renormalised individually. Of course, only the vacuum contribution to $\Sigma^{(1)}$ requires renormalisation, the corresponding counterterms being well known from vacuum QED,

$$e_x(n_0) = \frac{i}{2} \int \frac{d^4q}{(2\pi)^4} D_{\mu\nu}^0(q) \left[\Pi^{(0),\mu\nu}(q) - \Pi_V^{(0),\mu\nu}(q) \right] - i \int \frac{d^4p}{(2\pi)^4} \text{tr} \left[G_D^0(p) \Delta \Sigma_V^{(1)}(p) \right] \quad (\text{B.48})$$

As discussed in detail in Appendix A. the self energy counterterm $\Delta \Sigma_V^{(1)}(p)$ is defined so that the renormalised vacuum self energy $\Sigma_{V,R}(p)$ (A.45) satisfies the standard on-shell normalisation condition (A.40), i.e. on the 1-loop level one obtains (A.46). Using (B.2) $e_x(n_0)$ can thus be rewritten as

$$\begin{aligned}
 e_x(n_0) &= \frac{1}{2} \int \frac{d^4 q}{(2\pi)^4} \int \frac{d^4 p}{(2\pi)^4} D_{\mu\nu}^0(q) \operatorname{tr} \left[G_D^0(p+q) \gamma^\mu G_D^0(p) \gamma^\nu \right] \\
 &\quad - i \int \frac{d^4 p}{(2\pi)^4} \operatorname{tr} \left[G_D^0(p) \Sigma_{V,R}^{(1)}(p) \right] .
 \end{aligned}$$

The second term vanishes according to Eqs.(B.3,A.40),

$$\left[(\not{p} + m) \Sigma_{V,R}(p) \right]_{p^2 = \not{p}^2 = m^2} = 0 , \quad (\text{B.49})$$

so that the standard renormalisation scheme eliminates all vacuum corrections to $e_x(n_0)$ without the need to apply either the no-sea or the no-pair approximation. The first term, which is also obtained within both the no-sea and the no-pair approximation for $e_x(n_0)$, can be evaluated straightforwardly [93, 94, 95],

$$e_x(n_0) = e_x^{NRHEG}(n_0) \Phi_x(\beta) \quad (\text{B.50})$$

$$e_x^{NRHEG}(n_0) = -\frac{e^2}{4\pi^3} k_F^4 \quad (\text{B.51})$$

$$\Phi_x(\beta) = 1 - \frac{3}{2} \left[\frac{\eta}{\beta} - \frac{1}{\beta^2} \operatorname{arsinh}(\beta) \right]^2 . \quad (\text{B.52})$$

Using the decomposition (A.10) $e_x(n_0)$ can be split into a longitudinal and a transverse contribution [19, 95],

$$e_x^{L/T}(n_0) = e_x^{NRHEG}(n_0) \Phi_x^{L/T}(\beta) \quad (\text{B.53})$$

$$\Phi_x^L(\beta) = \frac{5}{6} + \frac{1}{3\beta^2} + \frac{2\eta}{3\beta} \operatorname{arsinh}(\beta) \quad (\text{B.54})$$

$$\begin{aligned}
 & - \frac{2\eta^4}{3\beta^4} \ln(\eta) - \frac{1}{2} \left(\frac{\eta}{\beta} - \frac{\operatorname{arsinh}(\beta)}{\beta^2} \right)^2 \\
 \Phi_x^T(\beta) &= \frac{1}{6} - \frac{1}{3\beta^2} - \frac{2\eta}{3\beta} \operatorname{arsinh}(\beta) \quad (\text{B.55}) \\
 & + \frac{2\eta^4}{3\beta^4} \ln(\eta) - \left(\frac{\eta}{\beta} - \frac{\operatorname{arsinh}(\beta)}{\beta^2} \right)^2 .
 \end{aligned}$$

The UV-renormalisation procedure is particularly involved for the correlation energy e_c . Most of the relevant counterterms provided by ΔE_{xc}^{RHEG} , however, are already included if the basic expression (B.45) is understood as being written in terms of the renormalised response function $\chi_{R,\lambda}^{\mu\nu}(q)$,

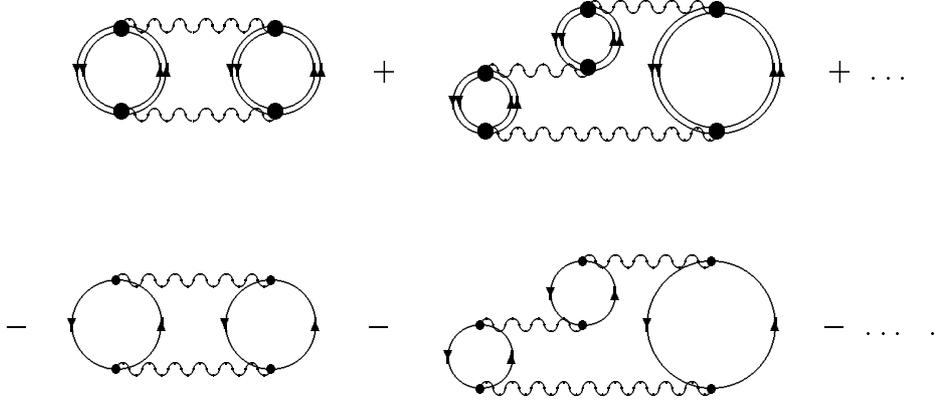
$$e_{xc}(n_0) = \frac{i}{2} \int_0^1 d\lambda \int \frac{d^4 q}{(2\pi)^4} D_{\mu\nu}^0(q) \left[\chi_{R,\lambda}^{\mu\nu}(q) - \chi_{V,R,\lambda}^{\mu\nu}(q) \right] + \Delta \tilde{E}_{xc}^{RHEG}, \quad (\text{B.56})$$

where the exchange energy has not been subtracted for brevity. The only remaining divergence (to be eliminated by $\Delta \tilde{E}_{xc}^{RHEG}$) originates from the outermost loop integration in (B.56). It is most easily discussed within the

so-called random phase (or ring) approximation (RPA) in which $\Pi_{L/T}$ is approximated by its 1-loop contribution [93, 119, 96],

$$e_{xc}^{RPA}(n_0) = \frac{i}{2} \int_0^1 d\lambda \int \frac{d^4q}{(2\pi)^4} \left[\frac{D^0(q) \Pi_L^{(0)}(q)}{1 - \lambda D^0(q) \Pi_L^{(0)}(q)} - 2 \frac{D^0(q) \Pi_T^{(0)}(q)}{1 + \lambda D^0(q) \Pi_T^{(0)}(q)} - 3 \frac{D^0(q) \Pi_{V,R}^{(0)}(q)}{1 - \lambda D^0(q) \Pi_{V,R}^{(0)}(q)} \right] + \Delta \tilde{E}_{xc}^{RHEG,RPA},$$

i.e. in addition to the exchange graph (B.46) included for brevity, $e_{xc}^{RPA}(n_0)$ consists of the following diagrams,



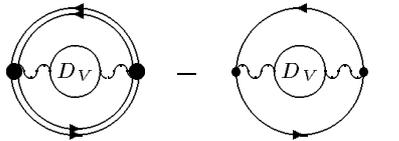
where the coupling constant integration is understood implicitly. The latter, however, can be easily performed to yield

$$e_{xc}^{RPA}(n_0) = -\frac{i}{2} \int \frac{d^4q}{(2\pi)^4} \left[\ln \left[1 - D_{V,R}(q) \Pi_{L,D}^{(0)}(q) \right] + 2 \ln \left[1 + D_{V,R}(q) \Pi_{T,D}^{(0)}(q) \right] \right] + \Delta \tilde{E}_{xc}^{RHEG,RPA}. \quad (\text{B.57})$$

At this point one usually defines the vacuum-screened exchange energy,

$$e_{x,s}(n_0) = \frac{i}{2} \int \frac{d^4q}{(2\pi)^4} \left[D_{V,R}(q) \Pi_{L,D}^{(0)}(q) - 2 D_{V,R}(q) \Pi_{T,D}^{(0)}(q) \right] + \Delta \tilde{E}_{xc}^{RHEG,RPA}, \quad (\text{B.58})$$

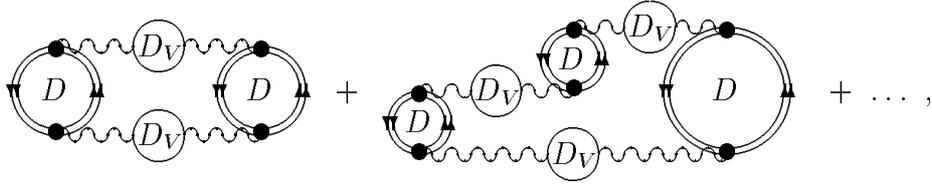
graphically given by



which requires renormalisation similar to its unscreened counterpart and, from a rigorous DFT point of view, is no longer a pure exchange contribution. Subtracting $e_{x,s}(n_0)$ from $e_{xc}^{RPA}(n_0)$ one ends up with a UV-convergent correlation energy [119],

$$e_{c,s}^{RPA}(n_0) = -\frac{i}{2} \int \frac{d^4q}{(2\pi)^4} \left[\ln \left[1 - D_{V,R}(q) \Pi_{L,D}^{(0)}(q) \right] \right. \\ \left. + 2 \ln \left[1 + D_{V,R}(q) \Pi_{T,D}^{(0)}(q) \right] \right. \\ \left. + D_{V,R}(q) \Pi_{L,D}^{(0)}(q) - 2D_{V,R}(q) \Pi_{T,D}^{(0)}(q) \right], \quad (\text{B.59})$$

as the lowest order diagram in (B.59) already contains $\Pi_{L/T,D}^{(0)}$ two times.²⁴ Diagrammatically (B.59) is given by



where the D inside the electron-loops indicates that only the electron gas part $\Pi_{D,\mu\nu}^{(0)}$ has to be inserted here. Finally, one can define the no-sea approximation of (B.59) by neglecting the screening effects due to the vacuum²⁵,

$$e_c^{L,RPA}(n_0) = -\frac{i}{2} \int \frac{d^4q}{(2\pi)^4} \left\{ \ln |1 - D^0(q) \Pi_{L,D}^{(0)}(q)| + D^0(q) \Pi_{L,D}^{(0)}(q) \right\} \quad (\text{B.60})$$

$$e_c^{T,RPA}(n_0) = -i \int \frac{d^4q}{(2\pi)^4} \left\{ \ln |1 + D^0(q) \Pi_{T,D}^{(0)}(q)| - D^0(q) \Pi_{T,D}^{(0)}(q) \right\}, \quad (\text{B.61})$$

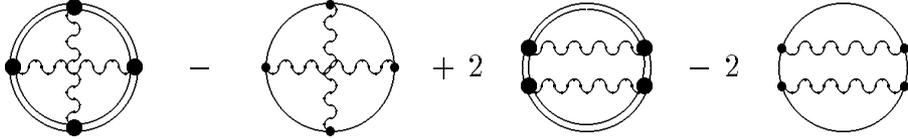
where $e_c^{RPA}(n_0)$ has also been decomposed into the longitudinal and the transverse parts using (B.33). $e_c^{L/T,RPA}(n_0)$ has been evaluated by Ramana and Rajagopal [98] as well as Müller and Serot [99]. The high-density (ultra-relativistic) limit e_c^{RPA} is [93, 96, 99]

²⁴ After Wick-rotation of q_0 in (B.59) one e.g. finds $\Pi_{L,D}^{(0)}(\mathbf{q}, iq_0) \sim (\mathbf{q}^2 + q_0^2)^{-1}$ and $\Pi_{V,R}^{(0)}(\mathbf{q}, iq_0) \sim (\mathbf{q}^2 + q_0^2) \ln |\mathbf{q}^2 + q_0^2|$ for large q^0 and $|\mathbf{q}|$ so that two factors of $\Pi_{L,D}^{(0)}(\mathbf{q}, iq_0)$ together with the required photon propagators are sufficient to insure UV-convergence of the outermost loop integral.

²⁵ Note that the definition of the no-sea approximation for (B.45) is somewhat arbitrary. As the guiding principle we have chosen to neglect all closed pure vacuum electron loops wherever they occur inside a diagram.

$$e_c^{RPA}(n_0) \xrightarrow{\beta \gg 1} \frac{e^4}{12\pi^4} k_F^4 \left(-7.796 \right) . \quad (\text{B.62})$$

In order to arrive at the complete the RPA+, which we understand as the combination of the RPA with the remaining second order (e^4) correlation contributions, the two second order exchange diagrams,



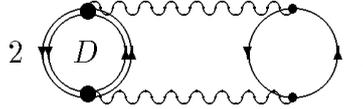
$$(\text{B.63})$$

have to be added to e_c^{RPA} . In contrast to the nonrelativistic situation the two right hand diagrams do not vanish. Both types of diagrams require renormalisation beyond the subtraction of their vacuum limit shown in Eq.(B.63). The complete density dependence of these diagrams is not known. In the ultrarelativistic limit one finds for the sum of both graphs (the individual contributions are not gauge invariant) [96]

$$e_c^{(x2)}(n_0) \xrightarrow{\beta \gg 1} \frac{e^4}{12\pi^4} k_F^4 \left(-3.18 \pm 0.12 \right) , \quad (\text{B.64})$$

so that their contribution constitutes about 40% of the RPA in this limit.

One can also analyse the 2-loop contribution to the screened exchange energy (B.58),



which in our definition is beyond the no-sea approximation. Its ultrarelativistic limit has been calculated by Freedman and McLerran [96],

$$e_{x,s}^{(2)}(n_0) \xrightarrow{\beta \gg 1} \frac{e^4}{12\pi^4} k_F^4 \left(\ln(2\beta) - \frac{11}{6} \right) . \quad (\text{B.65})$$

In the extreme high density limit $e_{x,s}^{(2)}$ thus dominates over all other known xc-energy contributions. Note, however, that the densities required for $e_{x,s}^{(2)}$ to be of the same order of magnitude as e_c^{RPA+} , i.e. $\beta \approx 10^3$, are not relevant for electronic structure calculations.

No calculations of e_c beyond the RPA+ are found in the literature. There is, however, a rather direct argument [99], which shows that the diagrammatic contributions discussed here are at least dominant in the high-density limit: As the relevant parameter for this limit is β , Eq.(B.39), it is completely equivalent to the zero mass limit. Taking the zero mass limit already from the very outset, i.e. basing the perturbation expansion for E_{xc} on an electron

propagator G^0 , Eq.(B.2), with $m = 0$, one can scale all loop-momenta in any given diagrammatic contribution to (B.45) by k_F and thereby extract an overall factor of k_F^4 . The remaining Feynman amplitudes are dimensionless and consequently *all* diagrams give contributions which are proportional to k_F^4 . The relative importance of the individual diagrams is thus essentially determined by their proportionality to α , apart from factors of $\ln|k_F/m|$ introduced by the renormalisation procedure (using m as natural renormalisation point) for vacuum parts of the diagrams. Therefore one would expect the RPA+ contributions together with $e_{x,s}^{(2)}$, Eq.(B.65), to be a rather accurate representation of E_{xc} for high densities $1 \ll \beta \ll 10^3$.

B.3 Pair Correlation Function

The relativistic pair correlation function g is defined in complete analogy to its nonrelativistic counterpart,

$$\lim_{y^0 \rightarrow x^0} i\chi^{00}(x, y) - n_0 \delta^{(3)}(\mathbf{x} - \mathbf{y}) = n_0 [g(\mathbf{x}, \mathbf{y}) - 1] n_0, \quad (\text{B.66})$$

which is an alternative form of Eq.(4.11) for the case of the RHEG. For relativistic homogeneous systems g in general depends on two variables, i.e. k_F and $|\mathbf{x} - \mathbf{y}|$, and two parameters, i.e. the coupling constant e^2 and the energy scale m . In the case of the RHEG, however, only its x-only limit (zeroth order in e^2) has been evaluated so far (compare the recent Monte Carlo study of g for the NRHEG [73]). Thus while the nonrelativistic $g_x^{NRHEG}(\mathbf{x}, \mathbf{y})$ is a function of $z = k_F |\mathbf{x} - \mathbf{y}|$ only,

$$g_x^{NRHEG}(z) = 1 - \frac{9}{2} \left[\frac{j_1(z)}{z} \right]^2, \quad (\text{B.67})$$

the corresponding x-only pair correlation function of the RHEG [102, 19],

$$\begin{aligned} g_x^{RHEG}(z, k_F) = & 1 - \frac{9}{4} \left[\frac{1}{\eta^2} \left(\sum_{i=0}^{\infty} \frac{j_{i+1}(z)}{z^{i+1}} \left(\frac{\beta}{\eta} \right)^{2i} \frac{(2i+1)!!}{2i+1} \right)^2 \right. \\ & + \frac{\beta^2}{\eta^2} \left(\sum_{i=0}^{\infty} \frac{j_{i+2}(z)}{z^{i+1}} \left(\frac{\beta}{\eta} \right)^{2i} \frac{(2i+1)!!}{2i+1} \right)^2 \\ & \left. + \left(\frac{j_1(z)}{z} \right)^2 \right] \end{aligned} \quad (\text{B.68})$$

in addition depends on β . The result (B.68) has been obtained within the no-pair approximation, i.e.

$$g_x^{RHEG} = 1 - \frac{i^2}{n_0^2} \int \frac{d^4 q}{(2\pi)^4} e^{iq \cdot (x-y)} \int \frac{d^4 p}{(2\pi)^4} \text{tr} \left[\gamma_0 G_D^0(p) \gamma_0 G_D^0(p-q) \right].$$

The series representation (B.68) of g_x^{RHEG} is not very suitable for actual applications of the RWDA. A simple and reasonably accurate fit to g_x^{RHEG} [92] is based on its form for $z = 0$,

$$g_x^{RHEG}(0, k_F) = \frac{3}{4} - \frac{9}{16} \left[\frac{\eta}{\beta^2} - \frac{\operatorname{arsinh}(\beta)}{\beta^3} \right]^2, \quad (\text{B.69})$$

with the limits

$$\lim_{\beta \rightarrow 0} g_x^{RHEG}(0, k_F) = \frac{1}{2} \quad (\text{B.70})$$

$$\lim_{\beta \rightarrow \infty} g_x^{RHEG}(0, k_F) = \frac{3}{4}. \quad (\text{B.71})$$

(B.71) may be interpreted as a consequence of the relativistic mixing of spin states [102]. The decreasing depth of the exchange hole $g_x^{RHEG} - 1$ with increasing β apparent from (B.70,B.71) is compensated by a broadening of the 'width' of the exchange hole (compare [102, 19]) in order to satisfy (4.13) in the homogeneous limit,

$$\frac{4}{3\pi} \int_0^\infty z^2 dz [g_x^{RHEG}(z, k_F) - 1] = -1. \quad (\text{B.72})$$

The scaling behavior required for (B.72) suggests the ansatz

$$g_x^{fit}(z, k_F) = 1 - \frac{9}{2} C_1(\beta) \left[\frac{j_1(C_2(\beta)z)}{C_2(\beta)z} \right]^2 \quad (\text{B.73})$$

$$C_1(\beta) = \frac{1}{2} + \frac{9}{8} \left[\frac{\eta}{\beta^2} - \frac{\operatorname{arsinh}(\beta)}{\beta^3} \right]^2 \quad (\text{B.74})$$

$$C_2(\beta) = C_1(\beta)^{\frac{1}{3}}, \quad (\text{B.75})$$

which not only approaches $g_x^{NRHEG}(z)$, Eq.(B.67), for vanishing β , but also satisfies Eqs.(B.69,B.72). The percentage deviation of $g_x^{fit}(z, k_F)$ from $g_x^{RHEG}(z, k_F)$ is plotted in Fig.B.1. In fact, even in the limit $\beta \rightarrow \infty$ in which

$$g_x^{RHEG}(z, \infty) = 1 - \frac{9}{4} \left[\left(2 \frac{j_1(z)}{z^2} - \frac{j_0(z)}{z^3} (2 + z^2) + \frac{2}{z^3} \right)^2 + \left(\frac{j_1(z)}{z^2} \right)^2 \right] \quad (\text{B.76})$$

the maximal error does not exceed 1%, while for the more relevant moderately high densities ($\beta < 0.5$ — at the r -expectation value of Hg⁷⁸⁺ one finds $\beta = 0.6$) the error reduces to less than 0.2%.

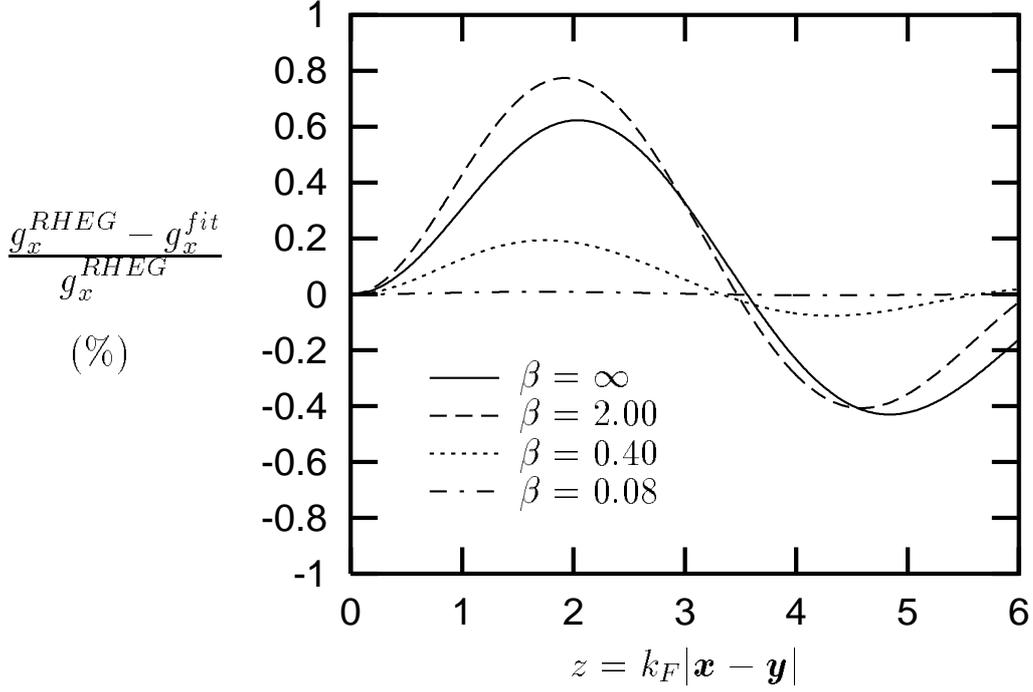


Fig. B.1. Percentage deviation of $g_x^{fit}(z, \beta)$, Eq.(B.73), from the exact $g_x^{RHEG}(z, \beta)$, Eq.(B.68), as a function of z for various values of β .

C. Weakly Inhomogeneous Electron Gas

Here we provide some details on inhomogeneous systems from the viewpoint of a weakly perturbed electron gas, i.e. we consider the external potential in the Hamiltonian (2.20) as a small perturbation. In this case one can expand the four current $\delta j^\mu(\mathbf{r})$ induced by a static perturbation in a power series with respect to $V^\mu(\mathbf{r})$,

$$\delta j_\mu(\mathbf{r}) = \sum_{n=1}^{\infty} \frac{e^n}{n!} \int d^3 r_1 \dots \int d^3 r_n \chi_{c, \mu \mu_1 \dots \mu_n}^{(n+1)}(\mathbf{r}, \mathbf{r}_1, \dots, \mathbf{r}_n) \quad (\text{C.1})$$

$$\times V^{\mu_1}(\mathbf{r}_1) \dots V^{\mu_n}(\mathbf{r}_n) + \Delta j_\mu(\mathbf{r}),$$

where $\chi_{c, \mu_1 \dots \mu_n}^{(n)}$ represents the connected static response functions²⁶ defined by (B.11) [120]. Of course, δj^μ satisfies current conservation,

$$\partial_\mu \delta j^\mu(\mathbf{r}) = \nabla \cdot \delta \mathbf{j}(\mathbf{r}) = 0 \quad \Rightarrow \quad \int d^3 r \delta j^0(\mathbf{r}) = 0, \quad (\text{C.2})$$

²⁶ Note, that (C.1) could be used as alternative definition for the static response functions.

which is directly related to the transversality of $\chi_{c,\mu_1\dots\mu_n}^{(n)}$ displayed in Eq.(B.13).

The induced current obtained from (C.1) is automatically UV-finite if the expansion is based on renormalised response functions, i.e. $\Delta j_\mu(\mathbf{r})$ just sums up the terms required for the transition from the $\chi_{c,\mu_1\dots\mu_n}^{(n)}$ to their renormalised counterparts. It is instructive to analyse the corresponding counterterms for the noninteracting limit of (C.1) given graphically by

$$-i \delta j_\mu^{(0)} = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3} + \dots \quad (\text{C.3})$$

(note the multiplicities contained in $\chi_{c,\mu_1\dots\mu_n}^{(n)}$) where the external potential has been represented by

$$e V_\rho(\mathbf{q}) = \text{Diagram 4} \quad (\text{C.4})$$

While the noninteracting 3-point function, i.e. the second graph, is UV-finite due to Furry's theorem, the noninteracting 4-point function (third diagram) is UV-finite due to gauge invariance and all higher order response functions are overall convergent. The only divergent term to be examined results from the relativistic Lindhard function. The corresponding counterterm has been discussed in Appendix A.. Using again dimensional regularisation one finds

$$\Delta j_\mu^{(0)}(\mathbf{r}) = -\frac{e}{12\pi^2} \Gamma\left(\frac{4-d}{2}\right) \nabla^2 V_\mu(\mathbf{r}) \quad , \quad (\text{C.5})$$

if the gauge $\nabla \cdot \mathbf{V}(\mathbf{r}) = 0$ is used.

The corresponding energy shift can be evaluated by a coupling constant integration with respect to the external potential. Scaling the external potential Hamiltonian by λ ,

$$\hat{H}_{ext}(\lambda) = \lambda e \int d^3r \hat{j}^\mu(\mathbf{r}) V_\mu(\mathbf{r}) \quad , \quad (\text{C.6})$$

one obtains for the corresponding ground state energy

$$E_{tot}(\lambda) = \langle \Phi_0(\lambda) | \hat{H}^{RHEG} + \hat{H}_{ext}(\lambda) | \Phi_0(\lambda) \rangle - \langle 0 | \hat{H}^{RHEG} | 0 \rangle + \Delta E_{tot}^{RHEG} + \Delta E_{tot}^{inhom}(\lambda) \quad , \quad (\text{C.7})$$

by a coupling constant integration approach (using a normalised ground state $|\Phi_0(\lambda)\rangle$ for given λ),

$$\begin{aligned}
 E_{tot}(\lambda = 1) &= E_{tot}^{RHEG} + e \int_0^1 d\lambda \int d^3r j^\mu(\lambda, \mathbf{r}) V_\mu(\mathbf{r}) + \Delta E_{tot}^{inhom}(\lambda = 1) \\
 &= E_{tot}^{RHEG} + e \int d^3r j^\mu(\lambda = 0, \mathbf{r}) V_\mu(\mathbf{r}) + \Delta E_{tot}^{inhom} \quad (C.8) \\
 &\quad + \sum_{n=2}^{\infty} \frac{e^n}{n!} \int d^3r_1 \dots \int d^3r_n \chi_{c, \mu_1 \dots \mu_n}^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n) \\
 &\quad \times V^{\mu_1}(\mathbf{r}_1) \dots V^{\mu_n}(\mathbf{r}_n) ,
 \end{aligned}$$

where (C.1) has been utilised for any given λ and $j^\mu(\lambda = 0, \mathbf{r}) = g^{\mu 0} n_0$ represents the current of the unperturbed system, i.e. the RHEG.

As for the induced four current the renormalisation of the inhomogeneity corrections to E_{tot}^{RHEG} reduces to the renormalisation of the $\chi_{c, \mu_1 \dots \mu_n}^{(n)}$. The counterterms are thus closely related to those for δj^μ ,

$$\Delta E_{tot}^{inhom} = e \int_0^1 d\lambda \int d^3r \Delta j^\mu(\lambda, \mathbf{r}) V_\mu(\mathbf{r}) . \quad (C.9)$$

The only counterterm on the noninteracting level, corresponding to (C.5), is e.g. given by

$$\Delta E_{tot}^{(0), inhom} = -\frac{e^2}{24\pi^2} \Gamma\left(\frac{4-d}{2}\right) \int d^3r V_\mu(\mathbf{r}) \nabla^2 V^\mu(\mathbf{r}) . \quad (C.10)$$

The counterterm (C.9) can be decomposed into contributions to the individual energy components. Again this is most easily demonstrated for the noninteracting case. Here the total energy is just a sum of the external potential energy,

$$E_{ext} = \int d^3r V^\mu(\mathbf{r}) \left[g^{\mu 0} n_0 + \delta j^\mu(\mathbf{r}) \right] + \Delta E_{ext}^{(0), inhom} , \quad (C.11)$$

which requires the counterterm

$$\Delta E_{ext}^{(0), inhom} = -\frac{e^2}{12\pi^2} \Gamma\left(\frac{4-d}{2}\right) \int d^3r V_\mu(\mathbf{r}) \nabla^2 V^\mu(\mathbf{r}) , \quad (C.12)$$

and the noninteracting kinetic contribution T_s which absorbs the remainder of (C.10),

$$\Delta T_s^{inhom} = \frac{e^2}{24\pi^2} \Gamma\left(\frac{4-d}{2}\right) \int d^3r V_\mu(\mathbf{r}) \nabla^2 V^\mu(\mathbf{r}) . \quad (C.13)$$

D. Linear Response Corrections to the Relativistic LDA

While the RLDA for $E_{xc}[j^\nu]$ is based on the xc-energy density of the RHEG, Eq.(B.45), the response expansions (C.1,C.8) allow the derivation of systematic corrections to the RLDA. We restrict ourselves here to the case of linear response for which the starting point is given by (C.1) to lowest order,

$$\delta j^\mu(\mathbf{q}) = e\chi^{\mu\nu}(q^0 = 0, \mathbf{q}) V_\nu(\mathbf{q}) \quad , \quad (\text{D.1})$$

($\chi^{\mu\nu}$ is always understood to be renormalised in this Appendix, so that counterterms are not displayed explicitly). Insertion of (D.1) into the lowest order contribution to (C.8) then leads to

$$\delta E_{tot}^{LR} = e \int \frac{d^3q}{(2\pi)^3} \delta j^\mu(\mathbf{q}) V_\mu(\mathbf{q}) - \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \delta j^\mu(\mathbf{q}) \chi_{\mu\nu}^{-1}(0, \mathbf{q}) \delta j^\nu(-\mathbf{q}).$$

Inserting the result (B.34) for the inverse response function,

$$\begin{aligned} \delta E_{tot}^{LR} = & \int \frac{d^3q}{(2\pi)^3} \left\{ e\delta j^\mu(\mathbf{q}) V_\mu(\mathbf{q}) + \frac{1}{2}\delta j^\mu(\mathbf{q}) D_L^0(\mathbf{q}) \delta j_\mu(-\mathbf{q}) \right\} \quad (\text{D.2}) \\ & - \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \delta j^\mu(\mathbf{q}) \Pi_{\mu\nu}^{-1}(0, \mathbf{q}) \delta j^\nu(-\mathbf{q}) \quad , \end{aligned}$$

one can identify the first term as the coupling to the external potential, the second as the induced Hartree energy. The third term involves the change in the kinetic energy δT_s^{LR} and the xc-energy δE_{xc}^{LR} , where the former is given by the noninteracting limit of $\Pi_{\mu\nu}^{-1}(\mathbf{q}, 0)$ so that the two contributions can be separated. Utilising the tensor structure of $\Pi_{\mu\nu}^{-1}(\mathbf{q}, 0)$, Eq.(B.35), one finally arrives at

$$\delta T_s^{LR} = -\frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \left\{ \frac{\delta j^0(\mathbf{q}) \delta j^0(-\mathbf{q})}{\Pi_L^{(0)}(0, \mathbf{q})} + \frac{[\hat{\mathbf{q}} \times \delta \mathbf{j}(\mathbf{q})] \cdot [\hat{\mathbf{q}} \times \delta \mathbf{j}(-\mathbf{q})]}{\Pi_T^{(0)}(0, \mathbf{q})} \right\} \quad (\text{D.3})$$

$$\begin{aligned} \delta E_{xc}^{LR} = & \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \left\{ \delta j^0(\mathbf{q}) \left[\frac{1}{\Pi_L^{(0)}(0, \mathbf{q})} - \frac{1}{\Pi_L(0, \mathbf{q})} \right] \delta j^0(-\mathbf{q}) \right. \quad (\text{D.4}) \\ & \left. + \left[\frac{1}{\Pi_T^{(0)}(0, \mathbf{q})} - \frac{1}{\Pi_T(0, \mathbf{q})} \right] [\hat{\mathbf{q}} \times \delta \mathbf{j}(\mathbf{q})] \cdot [\hat{\mathbf{q}} \times \delta \mathbf{j}(-\mathbf{q})] \right\}, \end{aligned}$$

where $\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}|$. At this point, δT_s^{LR} and δE_{xc}^{LR} are given as functionals of n_0 (inside $\Pi_{L/T}$) and δj^ν but not yet as functionals of the complete current $j^\nu = g^{\nu 0} n_0 + \delta j^\nu$. Two paths can be followed towards the construction of actual current density functionals: On the one hand, one can rewrite the complete linear response energies (D.3,D.4) as highly nonlocal current density functionals utilising either that $j^\nu(\mathbf{x}) - j^\nu(\mathbf{y}) = \delta j^\nu(\mathbf{x}) - \delta j^\nu(\mathbf{y})$ [5, 6] or that $\nabla j^\nu(\mathbf{x}) = \nabla \delta j^\nu(\mathbf{x})$ [121]. On the other hand, one can restrict oneself to a long-wavelength expansion of (D.3,D.4) assuming $\delta j^\nu(\mathbf{q})$ to be strongly

localised, i.e. $\delta j^\nu(\mathbf{x})$ to be rather delocalised. This approach leads to (semilocal) gradient corrections and has been pursued extensively in the case of the nonrelativistic $E_{xc}[j^\nu]$. However, due to the limited information available for the relativistic polarisation functions $\Pi_{L/T}$ (and even on their small- \mathbf{q} expansions) no applications of (D.4) have been reported so far.

In order to illustrate the derivation of gradient corrections we thus consider $T_s[j^\nu]$. Extracting the long-wavelength limit of (D.3),

$$\delta T_s^{[0]} = -\frac{1}{2} \int \frac{d^3 q}{(2\pi)^3} \frac{\delta j^0(\mathbf{q}) \delta j^0(-\mathbf{q})}{\Pi_L^{(0)}(0, \mathbf{0})}, \quad (\text{D.5})$$

which is absorbed in the RLDA in accordance with the compressibility sum rule, one finds by insertion of (B.36-B.38) into (D.3) and subsequent Fourier transformation,

$$\begin{aligned} \delta T_s^{[2]} &= \frac{1}{72m} \int d^3 x \frac{1}{n_0 \eta} \left[1 + 2 \frac{\beta}{\eta} \text{arsinh}(\beta) \right] \left[\nabla \delta j^0(\mathbf{x}) \right]^2 \\ &\quad + \frac{3\pi}{4} \int d^3 x \int d^3 y \frac{1}{\text{arsinh}(\beta)} \frac{\delta \mathbf{j}(\mathbf{x}) \cdot \delta \mathbf{j}(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \\ \delta T_s^{[4]} &= \frac{1}{4320m} \int d^3 x \frac{1}{n_0 k_F^2 \eta} \left[\nabla^2 \delta j^0(\mathbf{x}) \right]^2 \\ &\quad \times \left[5 \left(1 + 2 \frac{\beta}{\eta} \text{arsinh}(\beta) \right)^2 + 3(1 - 4\beta^2) + 12 \frac{\beta^3}{\eta} \right] \\ &\quad + \frac{3\pi^2}{10m^2} \int d^3 x \frac{1}{\text{arsinh}(\beta)^2} \left(\frac{\eta}{\beta} - 1 \right) \delta \mathbf{j}(\mathbf{x}) \cdot \delta \mathbf{j}(\mathbf{x}), \end{aligned}$$

where current conservation has been used and $[k]$ denotes the order of the small- \mathbf{q} expansion. For the density components of $\delta T_s^{[2/4]}$ (i.e. the first and third line) one now can simply replace $\nabla \delta j^0(\mathbf{x}) = \nabla j^0(\mathbf{x})$ and, correct to second order, $k_F = [3\pi^2 j^0(\mathbf{x})]^{1/3}$. While one can also utilise $\delta \mathbf{j}(\mathbf{x}) = \mathbf{j}(\mathbf{x})$, the density dependent prefactor $1/\text{arsinh}(k_F/m)$ of the first current component can not be expressed unambiguously in terms of $j^0(\mathbf{x})$ as now two spatial variables are available. Similar to the situation for the complete linear response corrections (D.3,D.4) one is left with a choice for this substitution²⁷. Abbreviating this (symmetric) function of \mathbf{x} and \mathbf{y} by $\bar{\beta}(\mathbf{x}, \mathbf{y})$ one thus obtains

$$\begin{aligned} \delta T_s^{[2]}[j^\nu] &= \frac{m^2}{24\pi^2} \int d^3 x (\nabla \beta)^2 \frac{\beta}{\eta} \left[1 + 2 \frac{\beta}{\eta} \text{arsinh}(\beta) \right] \\ &\quad + \frac{3\pi}{4} \int d^3 x \int d^3 y \frac{1}{\text{arsinh}(\bar{\beta}(\mathbf{x}, \mathbf{y}))} \frac{\mathbf{j}(\mathbf{x}) \cdot \mathbf{j}(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \end{aligned} \quad (\text{D.6})$$

²⁷ In contrast to the linear response approach the direct gradient expansion of $T_s[j^\mu]$ determines the current contribution to the second order gradient correction completely [122].

$$\begin{aligned}
\delta T_s^{[4]}[j^\nu] &= \frac{1}{1440\pi^2} \int d^3x \frac{(\nabla^2\beta)^2}{\beta\eta} \\
&\quad \times \left[5 \left(1 + 2\frac{\beta}{\eta} \operatorname{arsinh}(\beta) \right)^2 + 3(1 - 4\beta^2) + 12\frac{\beta^3}{\eta} \right] \\
&\quad + \frac{3\pi^2}{10m^2} \int d^3x \frac{1}{\operatorname{arsinh}(\beta)^2} \left(\frac{\eta}{\beta} - 1 \right) \mathbf{j}(\mathbf{x})^2 \quad ,
\end{aligned} \tag{D.7}$$

where β is understood as $\beta = [3\pi^2 j^0(\mathbf{x})]^{1/3}/m$ ($\eta = \sqrt{1 + \beta^2}$). One should note that the vacuum parts of $\Pi_{L/T}^{(0)}$ are responsible for the rightmost terms in both the density and the current component of $\delta T_s^{[4]}$. We also remark that the response approach can be extended to quadratic and cubic response which allows the derivation of the complete gradient expansion to fourth order [60].

E. Direct Gradient Expansion of $T_s[j^\nu]$

A density (or current density) functional representation of the relativistic noninteracting kinetic energy T_s can either be obtained by the (linear) response technique discussed in Appendix D. or by a direct gradient expansion (GE) on the basis of (2.38), whose kinetic contribution is given by

$$\begin{aligned}
T_s &= -i \int d^3x \lim_{y \rightarrow x} \operatorname{tr} \left[\left(-i\boldsymbol{\gamma} \cdot \nabla + m \right) G(x, y) \right] \\
&\quad - \langle 0 | \hat{H}_e | 0 \rangle + \Delta T_s^{\text{inhom}} \quad .
\end{aligned} \tag{E.1}$$

The Greens function involved in (E.1) is the propagator for a given external potential V^μ (here to be understood as the KS-potential), which has already been discussed in Section 2.. It satisfies the differential equation

$$\left(i\boldsymbol{\not{\partial}}_x - m - V(\mathbf{x}) \right) G(x, y) = \delta^{(4)}(x - y) \quad , \tag{E.2}$$

(a factor of e has been absorbed into V^μ for brevity) and can be expanded in powers of V^μ in the form (2.36) without requiring renormalisation.

In order to set up the GE for $T_s[j^\nu]$ one proceeds in four steps [123]. In the first step the differential equation (E.2) is solved by an expansion in powers of gradients of V^μ . The starting point of this expansion is the known solution of (E.2) for a constant external potential,

$$G^{[0]}(x, y) = e^{-i(x-y) \cdot V} \int \frac{d^4p}{(2\pi)^4} e^{-ip \cdot (x-y)} G^{[0]}(p_\mu, V_\nu) \tag{E.3}$$

$$G^{[0]}(p_\mu, V_\nu) = G_V^0(p) - 2\pi i (\boldsymbol{\not{p}} + m) \frac{\delta(p^0 - E)}{2E} \Theta(\epsilon_F - V^0 - p^0) \quad . \tag{E.4}$$

The complete expansion is then written in the form

$$G(x, y) = e^{-i(x-y) \cdot V(x)} \int \frac{d^4 p}{(2\pi)^4} e^{-ip \cdot (x-y)} \sum_{k=0}^{\infty} G^{[k]}(p_\mu, V_\nu(\mathbf{x})) \quad , \quad (\text{E.5})$$

where $[k]$ denotes the order of the gradients and an overall phase factor has been extracted in analogy to (E.3). For $x^0 = y^0$ (E.5) coincides with an expansion in powers of \hbar and is therefore called a semiclassical expansion. Upon insertion into (E.2) the form (E.5) leads to the recursion relation

$$(\not{p} - m)G^{[k]}(p_\mu, V_\nu(\mathbf{x})) = \left[(i\not{p}V_\nu(\mathbf{x})) \frac{\partial}{\partial p_\nu} - i\not{p} \right] G^{[k-1]}(p_\mu, V_\nu(\mathbf{x})) \quad , \quad (\text{E.6})$$

whose solution with appropriate boundary conditions is given by

$$G^{[k]}(p_\mu, V_\nu) = \left\{ G^{[0]}(p_\mu, V_\nu) \left[(i\not{p}V_\nu) \frac{\partial}{\partial p_\nu} - i\not{p} \right] \right\}^k G^{[0]}(p_\mu, V_\nu) \quad . \quad (\text{E.7})$$

(E.7) is then evaluated explicitly to the (finite) order of gradients one is interested in.

In a second step the semiclassical expansion (E.7) is used to evaluate the semiclassical expansions of the four current j^ν , Eq.(2.39), and of T_s , Eq.(E.1). The symmetric limits in (2.39) and (E.1) introduce UV-divergencies which are eliminated by the corresponding counterterms $\Delta j^{\nu,(0)}$ and ΔT_s^{inhom} (as discussed in Section 2.).

In order to illustrate this point explicitly, we consider the expansion of $j^0(\mathbf{x}) = n(\mathbf{x})$ and $T_s[n]$ for the case of a purely electrostatic potential $V^\mu = (V, \mathbf{0})$ to second order in the gradients of V . Using dimensional regularisation for the evaluation of the integrals in question one finds for the semiclassical expansions without counterterms,

$$\tilde{n}[V]_{reg} = \frac{p^3}{3\pi^2} + \frac{1}{12\pi^2} \Gamma \left(2 - \frac{d}{2} \right) (\nabla^2 V) \quad (\text{E.8})$$

$$\begin{aligned} & - \frac{1}{12\pi^2} \left\{ \left[\frac{E}{p} + 2 \operatorname{arsinh} \left(\frac{p}{m} \right) \right] (\nabla^2 V) + \left[\frac{E^2}{p^2} - 3 \right] \frac{(\nabla V)^2}{2p} \right\} \\ \tilde{t}_s[V]_{reg} & = \frac{m^4}{16\pi^2} \Gamma \left(2 - \frac{d}{2} \right) + \frac{1}{8\pi^2} \left\{ pE^3 + p^3 E - \operatorname{arsinh} \left(\frac{p}{m} \right) \right\} \quad (\text{E.9}) \\ & + \frac{1}{24\pi^2} \Gamma \left(2 - \frac{d}{2} \right) (\nabla V)^2 - \frac{1}{12\pi^2} \left[\frac{E^2}{p} + p \right] (\nabla^2 V) \\ & - \frac{1}{12\pi^2} \left[\frac{E^3}{2p^3} - \frac{E}{p} + \operatorname{arsinh} \left(\frac{p}{m} \right) \right] (\nabla V)^2, \end{aligned}$$

where

$$E = \epsilon_F - V(\mathbf{x}) \quad ; \quad p = \sqrt{E^2 - m^2} \Theta(E^2 - m^2) \quad . \quad (\text{E.10})$$

One recognises divergent contributions (in the limit $d \rightarrow 4$), namely the divergent contribution of the kinetic energy of the Dirac sea

$$\begin{aligned} \langle 0|\hat{\mathcal{H}}_e|0\rangle &= -i \lim_{y \rightarrow x} \text{tr} \left[\left(-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m \right) G_V^0(x, y) \right] \\ &= \frac{m^4}{16\pi^2} \Gamma \left(2 - \frac{d}{2} \right), \end{aligned} \quad (\text{E.11})$$

and the UV-divergencies arising from taking the symmetric limit, which are proportional to $\boldsymbol{\nabla}^2 V$. While the former is eliminated by the subtraction of the vacuum energy of noninteracting fermions according to (E.1), the UV-divergencies are cancelled by the counterterms $\Delta j^{\nu, (0)}$ and ΔT_s^{inhom} , given in Eqs.(C.5,C.13). One thus explicitly verifies that from (E.8,E.9) finite semiclassical expansions $\tilde{n}[V]$ and $\tilde{t}_s[V]$ are obtained,

$$\tilde{n}[V] = \tilde{n}[V]_{reg} + \Delta j^{0, (0)} \quad (\text{E.12})$$

$$\tilde{T}_s[V] = \int d^3x \tilde{t}_s[V]_{reg} - \langle 0|\hat{H}_e|0\rangle + \Delta T_s^{inhom}. \quad (\text{E.13})$$

In the third step the semiclassical expansion of j^ν is inverted order by order to the order required. This yields V^ν as a function of j^ν and its gradients, so that by insertion into the semiclassical expansion for T_s (the fourth step) one obtains the desired relativistic gradient expansion (RGE). For the example considered here ($\mathbf{V} = \mathbf{0}$) this leads to [21]

$$T_s^{RGE0}[n] = \int d^3x t_s^{NRHEG}(n) \Phi_{s,0}(\beta) \quad (\text{E.14})$$

$$T_s^{RGE2}[n] = \frac{1}{72m} \int d^3x \frac{(\boldsymbol{\nabla} n)^2}{n} \Phi_{s,2}(\beta) \quad (\text{E.15})$$

$$\Phi_{s,2}(\beta) = \frac{1}{\eta} \left[1 + 2 \frac{\beta}{\eta} \text{arsinh}(\beta) \right], \quad (\text{E.16})$$

where the electron rest mass has been subtracted and t_s^{NRHEG} and $\Phi_{s,0}$ are given by (B.43,B.44). The relativistic correction factors $\Phi_{s,0/2}$ are plotted in Fig.E.1. In contrast to $\Phi_{x,c}$ both $\Phi_{s,0}$ and $\Phi_{s,2}$ decrease in the ultrarelativistic limit.

The fourth order correction corresponding to a purely electrostatic potential has also been evaluated [124],

$$\begin{aligned} T_s^{RGE4}[n] &= \int d^3x \left[t_{s,V}^{RGE4}[n] + t_{s,D}^{RGE4}[n] \right] \\ t_{s,V}^{RGE4} &= \frac{1}{360\pi^2} \left\{ 3 \frac{\beta^2}{\eta^2} (\boldsymbol{\nabla}^2 \beta)^2 + 6 \frac{\beta}{\eta^4} (\boldsymbol{\nabla}^2 \beta) (\boldsymbol{\nabla} \beta)^2 + \frac{3 - \beta^4 \eta^2}{\eta^6} (\boldsymbol{\nabla} \beta)^4 \right\} \\ t_{s,D}^{RGE4} &= \frac{1}{5760\pi^2} \left\{ 4 \frac{(\boldsymbol{\nabla}^2 \beta)^2}{\beta \eta} \left[3(1 - 4\beta^2) + 5 \left(1 + 2 \frac{\beta}{\eta} \text{arsinh}(\beta) \right)^2 \right] \right\} \end{aligned}$$

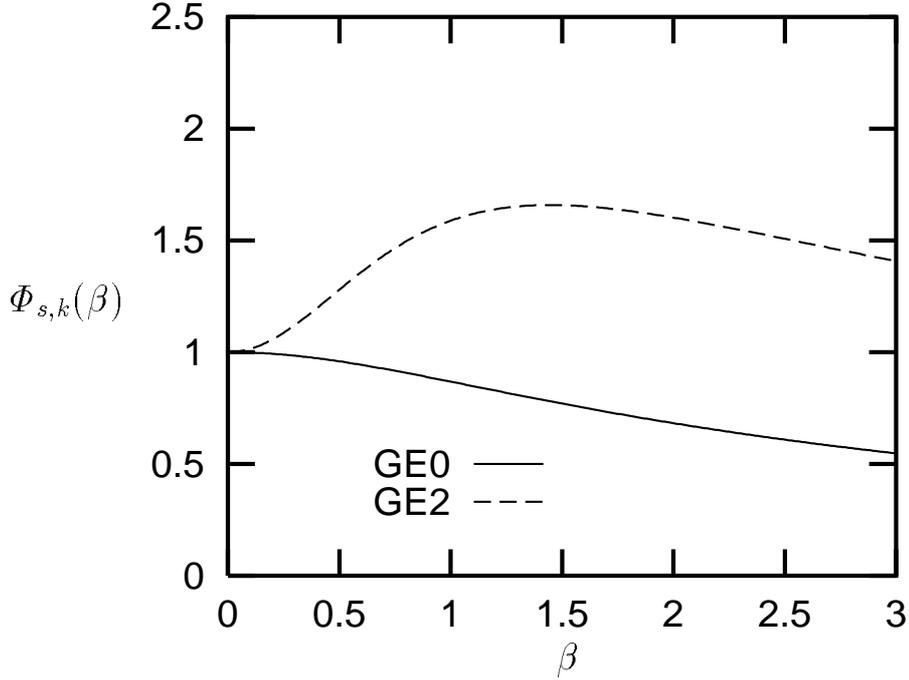


Fig. E.1. Relativistic corrections to kinetic energy densities. Eq.(B.44) — solid line (GE0), Eq.(E.16) — dashed line (GE2).

$$\begin{aligned}
& + 2 \frac{(\nabla^2 \beta)(\nabla \beta)^2}{\beta^2 \eta^3} \left[-41\beta^2 + 20 \left(1 + 2 \frac{\beta}{\eta} \operatorname{arsinh}(\beta) \right) \right. \\
& \quad \left. \times \left(\frac{\beta^2 + \eta^2}{2} + 2 \frac{\beta}{\eta} \operatorname{arsinh}(\beta) \right) \right] \\
& + \frac{(\nabla \beta)^4}{\beta^3 \eta^5} \left[3 - 19\beta^2 - 8\beta^4 + 8\beta^6 + 16\beta^8 \right. \\
& \quad \left. + 20 \left(\frac{\beta^2 + \eta^2}{2} + 2 \frac{\beta}{\eta} \operatorname{arsinh}(\beta) \right)^2 \right] \Big\} .
\end{aligned}$$

The lowest order term $T_s^{RGE0}[n]$, the relativistic kinetic energy in the Thomas-Fermi limit, has first been calculated by Vallarta and Rosen [12]. In the second order contribution (which is given in a form simplified by partial integration) explicit vacuum corrections do not occur after renormalisation. Finite radiative corrections, originating from the vacuum part of the propagator (E.5), first show up in fourth order, where the term in $t_{s,V}^{RGE4}$ proportional to $(\nabla \beta)^4$ can be identified with the electrostatic part of the Euler-Heisenberg energy of QED [26]. One also recognises that both $T_s^{RGE2}[n]$ and the linear response component of $T_s^{RGE4}[n]$ agree with the results (D.6,D.7). In the nonrelativistic limit the individual contributions reduce to the appropriate results of the nonrelativistic gradient expansion [125, 126, 127].

The direct gradient expansion has also been applied to evaluate the current dependence of T_s to second order [122],

$$\begin{aligned}
T_s^{RGE2}[\mathbf{j}] &= \frac{3}{16} \int d^3x \frac{1}{\operatorname{arsinh}(\beta(\mathbf{x}))} \\
&\quad \times \int d^3y \int d^3z \sum_{k,l=1}^3 \frac{\partial_k^y j^l(\mathbf{y}) \partial_k^z j^l(\mathbf{z}) - \partial_k^y j^l(\mathbf{y}) \partial_l^z j^k(\mathbf{z})}{|\mathbf{x} - \mathbf{y}| |\mathbf{x} - \mathbf{z}|}.
\end{aligned} \tag{E.17}$$

The direct GE provides an unambiguous result for $T_s^{RGE2}[\mathbf{j}]$ in contrast to the linear response approach as here no expansion in powers of V^μ itself is involved. Neglecting the \mathbf{x} -dependence of β one can reduce (E.17) to the current component of (D.6).

References

1. Jones R O, Gunnarsson O (1989) *Rev Mod Phys* 61: 689
2. Becke A D, (1992) *J Chem Phys* 96: 2155
3. Johnson B G, Gill P M W, Pople J A (1993) *J Chem Phys* 98: 5612
4. Gross E K U, Dreizler R M (eds) (1995) *Density Functional Theory. NATO ASI Series B, Vol 337*, Plenum, New York
5. Hohenberg P, Kohn W (1964) *Phys Rev* 136 B: 864
6. Kohn W, Sham L J (1965) *Phys Rev* 140 A: 1133
7. Eliav E, Kaldor U, Ishikawa Y (1994) *Phys Rev A* 49: 1724
8. Pyykkö P (1988) *Chem Rev* 88: 563
9. Pepper M, Bursten B E (1991) *Chem Rev* 91: 719
10. Becke A D (1988) *Phys Rev A* 38: 3098
11. Perdew J P (1991) In: Ziesche P, Eschrig H (eds) *Electronic Structure of Solids 1991*. Akademie Verlag, Berlin
12. Vallarta M S, Rosen N (1932) *Phys Rev* 41: 708
13. Jensen H (1933) *Z Phys* 82: 794
14. Thomas L H (1927) *Proc Cambridge Phil Soc* 23: 542
15. Fermi E (1928) *Z Phys* 48: 73
16. Gross E K U, Dreizler R M (1981) *Phys Lett* 81A: 447
17. Rajagopal A K, Callaway J (1973) *Phys Rev B* 7: 1912
18. Rajagopal A K (1978) *J Phys C* 11: L943
19. MacDonald A H, Vosko S H (1979) *J Phys C* 12: 2977
20. Malzacher P, Dreizler R M (1986) *Z Phys D* 2: 37
21. Engel E, Dreizler R M (1987) *Phys Rev A* 35: 3607
22. Engel E, Müller H, Speicher C, Dreizler R M (1995) In: Ref.[4], p 65
23. Liberman D, Waber J T, Cromer D T (1965) *Phys Rev* 137 A: 27
24. Andersen O K (1970) *Phys Rev B* 2: 883
25. Ramana M V, Rajagopal A K (1983) *Adv Chem Phys* 54: 231
26. Itzykson C, Zuber J-B (1980) *Quantum Field Theory*. McGraw-Hill, New York
27. Källén A O G (1958) In: *Handbuch der Physik, Band V, Teil 1*. Springer, Berlin
28. Schmutzer E (1972) *Symmetrien und Erhaltungssätze der Physik*. Akademie, Berlin
29. Bjorken J D, Drell S D (1965) *Relativistic Quantum Fields*. McGraw-Hill, New York, chap 14.6
30. Ramana M V, Rajagopal A K (1981) *J Phys C* 14: 4291
31. Plunien G, Müller B, Greiner W (1986) *Phys Rep* 134: 87

32. Rafelski J, Fulcher L P, Klein A (1978) Phys Rep 38C: 227
33. Greiner W, Müller B, Rafelski J (1985) Quantum Electrodynamics of Strong Fields. Springer, Berlin
34. Schweber S S (1966) Relativistic Quantum Field Theory. Harper, New York
35. Shadwick B A, Talman J D, Norman M R (1989) Comp Phys Commun 54: 95
36. Engel E, Keller S, Facco Bonetti A, Müller H, Dreizler R M (1995) Phys Rev A 52: 2750
37. Vignale G, Rasolt M (1987) Phys Rev Lett 59: 2360
38. Vignale G, Rasolt M (1988) Phys Rev B 37: 10685
39. For recent comparisons of QED results for atomic systems with experimental data see eg Chen M H, Cheng K T, Johnson W R (1993) Phys Rev A 47: 3692; Riis E, Sinclair A G, Poulsen O, Drake G W F, Rowley W R C, Levick A P (1994) Phys Rev A 49: 207
40. Ramana M V, Rajagopal A K (1979) J Phys C 12: L845
41. MacDonald A H (1983) J Phys C 16: 3869
42. Xu B X, Rajagopal A K, Ramana M V (1984) J Phys C 17: 1339
43. Eschrig H, Seifert G, Ziesche P (1985) Solid State Commun 56: 777
44. Diener G, Gräfenstein J (1989) J Phys Condens Matter 1: 8445
45. Nagy A (1994) Phys Rev A 49: 3074
46. Engel E, Dreizler R M (1988) Phys Rev A 38: 3909
47. Dreizler R M, Gross E K U (1990) Density Functional Theory. Springer, Berlin
48. Mann J B, Johnson W R (1971) Phys Rev A 4: 41
49. Parpia F A, Johnson W R (1984) J Phys B 17: 531
50. Parpia F A, Johnson W R (1983) J Phys B 16: L375
51. Parpia F A, Johnson W R (1983) Phys Lett 99 A: 172
52. Talman J D, Shadwick W F (1976) Phys Rev A 14: 36
53. Sharp R T, Horton G K (1953) Phys Rev 90: 317
54. Sahní V, Gruenebaum J, Perdew J P (1982) Phys Rev B 26: 4371
55. Langreth D C, Mehl M J (1983) Phys Rev B 28: 1809
56. Sham L J (1985) Phys Rev B 32: 3876
57. Engel E, Chevary J A, Macdonald L D, Vosko S H (1992) Z Phys D 23: 7
58. Krieger J B, Li Y, Iafrate G J (1992) Phys Rev B 45: 101
59. Engel E, Vosko S H (1993) Phys Rev A 47: 2800
60. Engel E, Vosko S H (1994) Phys Rev A 50: 10498
61. Kotani T (1994) Phys Rev B 50: 14816
62. Kotani T (1995) Phys Rev Lett 74: 2989
63. Bylander D M, Kleinman L (1995) Phys Rev Lett 74: 3660
64. Grabo T, Gross E K U (1995) Chem Phys Lett 240: 141
65. Krieger J B, Li Y, Iafrate G J (1990a) Phys Lett 146 A: 256
66. Krieger J B, Li Y, Iafrate G J (1990b) Phys Lett 148 A: 470
67. Li Y, Krieger J B, Norman M R, Iafrate G J (1991) Phys Rev B 44: 10437
68. Dylla K G, Grant I P, Johnson C T, Parpia F A, Plummer E P (1989) Comp Phys Commun 55: 425
69. In all our calculations the nuclei were represented by uniformly charged spheres with nuclear radii given by $R_{nucl} = 1.0793 A^{1/3} + 0.73587 fm$, A being the atomic mass (weighted by isotopic abundances) taken from Table III.7 of Ref.[128] unless explicitly stated otherwise. The speed of light has been set to $c = 137.0359895$.
70. Vosko S H, Wilk L, Nusair M (1980) Can J Phys 58: 1200
71. Perdew J P, Zunger A (1981) Phys Rev B 23: 5048
72. Perdew J P, Wang Y (1991) Phys Rev B 45: 13244
73. Ortiz G, Ballone P (1994) Phys Rev B 50: 1391
74. Ceperley D M, Alder B J (1980) Phys Rev Lett 45: 566

75. Ma S-K, Brueckner K A (1968) *Phys Rev* 165: 18
76. Sham L J (1971) In: Marcus P M, Janak J F, Williams A R (eds) *Computational Methods in Band Theory*. Plenum, New York, p 458
77. Geldart D J W, Rasolt M (1976) *Phys Rev B* 13: 1477
78. Antoniewicz P R, Kleinman L (1985) *Phys Rev B* 31: 6779
79. Kleinman L, Lee S (1988) *Phys Rev B* 37: 4634
80. Chevary J A, Vosko S H (1990) *Phys Rev B* 42: 5320
81. Engel E, Vosko S H (1990) *Phys Rev B* 42: 4940; *Phys Rev B* 44: 1446(E)
82. Bagno P, Jepsen O, Gunnarsson O (1989) *Phys Rev B* 40: 1997
83. Langreth D C, Mehl M J (1981) *Phys Rev Lett* 47: 446
84. Becke A D (1986) *J Chem Phys* 84: 4524
85. Perdew J P, Wang Y (1986) *Phys Rev B* 33: 8800
86. Perdew J P (1986) *Phys Rev B* 33: 8822; *Phys Rev B* 34: 7406(E)
87. Garcia A, Elsässer Ch, Zhu J, Louie S G, Cohen M L (1992) *Phys Rev B* 46: 9829; *Phys Rev B* 47: 4150(E)
88. Singh D J, Ashkenazi J (1992) *Phys Rev B* 46: 11570
89. Singh D J (1993) *Phys Rev B* 48: 14099
90. Dufek P, Blaha P, Sliwko V, Schwarz K (1994) *Phys Rev B* 49: 10170
91. Dufek P, Blaha P, Schwarz K (1994) *Phys Rev B* 50: 7279
92. Keller S (1988) Diploma thesis, Frankfurt/Main
93. Akhiezer I A, Peletminskii S V (1960) *Sov Phys JETP* 11: 1316
94. Zapolsky H S (1960) Cornell University LNS Report. unpublished
95. Jancovici B (1962) *Nuovo Cim XXV*: 428
96. Freedman B A, McLerran L D (1977) *Phys Rev D* 16: 1130, 1147, 1169
97. Ramana M V, Rajagopal A K, Johnson W R (1982) *Phys Rev A* 25: 96
98. Ramana M V, Rajagopal A K (1981) *Phys Rev A* 24: 1689
99. Müller H, Serot B D (1995) unpublished
100. Gunnarsson O, Jonson M, Lundqvist B I (1977) *Solid State Commun* 24: 765
101. Alonso J A, Girifalco L A (1978) *Phys Rev B* 17: 3735
102. Ellis D E (1977) *J Phys B* 10: 1
103. A simple scheme to overcome this problem has been suggested in Przybylski H, Borstel G (1984) *Solid State Commun* 49: 317; *Solid State Commun* 52: 713
104. Das M P, Ramana M V, Rajagopal A K (1980) *Phys Rev A* 22: 9
105. MacDonald A H, Daams J M, Vosko S H, Koelling D D (1981) *Phys Rev B* 23: 6377
106. Engel E, Vosko S H (1993) *Phys Rev B* 47: 13164
107. Davidson E R, Hagstrom S A, Chakravorty S J, Meiser Umar V, Froese Fischer C (1991) *Phys Rev A* 44: 7071
108. Ishikawa Y, Koc K (1994) *Phys Rev A* 50: 4733
109. Chakravorty S J, Gwaltney S R, Davidson E R, Parpia F A, Froese Fischer C (1993) *Phys Rev A* 47: 3649
110. Stroucken H J A C, Dreizler R M (1991) *Phys Rev A* 43: 3401
111. Rieger M M, Vogl P (1995) *Phys Rev A* 52: 282
112. t'Hooft G, Veltman M (1972) *Nucl Phys B* 44: 189
113. Landsman N P, van Weert Ch G (1987) *Phys Rep* 145: 141
114. Lim K, Horowitz C J (1989) *Nucl Phys A* 501: 729
115. Källén G, Sabry A (1955) *Dan Mat Fys Medd* 29: No.17
116. Barbieri R, Remiddi E (1973) *Nuovo Cim A* 13: 99
117. Kapusta J I (1989) *Finite-temperature Field Theory*. Cambridge Univ. Press, Cambridge
118. Braaten E, Pisarski R D (1990) *Nucl Phys B* 337: 569
119. Chin S A (1977) *Ann Phys (NY)* 108: 301

120. Brovman E G, Kagan Y (1969) Zh Eksp Teor Fiz 57: 1329 [Sov Phys JETP 30: 721 (1970)]
121. Engel E (1995) Phys Rev A 51: 1159
122. Müller H, Engel E, Dreizler R M (1989) Phys Rev A 40: 5542
123. Engel E, Müller H, Dreizler R M (1989) Phys Rev A 39: 4873
124. Pohlner W F, Dreizler R M (1991) Phys Rev A 44: 7165
125. Kirzhnits D A (1967) Field Theoretical Methods in Many-Body Systems. Pergamon, London
126. Hodges C H (1973) Can J Phys 51: 1428
127. Jennings B K (1973) PhD Thesis, McMaster University; Brack M, Jennings B K, Chu Y H (1976) Phys Lett 65B: 1
128. Hisaka K, et al. (Particle Data Group) (1992) Phys Rev D 45: Number 11, Part II