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# Correlated Effective Single-Particle Theory: Relativistic Optimized-Potential Method

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## Abstract

We analyze the relativistic exchange-correlation ( $xc$ ) energy functional  $E_{xc}$  of density functional theory (DFT), extending the conventional approach to  $E_{xc}$ , explicitly based on the density, by the concept of orbital-dependent representations. We introduce two different schemes for the derivation of  $xc$ -functionals depending on Kohn-Sham orbitals. On the one hand, a perturbation expansion, using the Kohn-Sham Hamiltonian as noninteracting reference system, allows to derive a perturbation expansion of  $E_{xc}$  in powers of  $e^2$ . Alternatively, the adiabatic connection formalism directly yields an RPA-like  $xc$ -functional. The  $xc$ -potential corresponding to these orbital-dependent functionals can be evaluated via the optimized-potential-method (OPM), which is also presented. The atomic exchange-only ground state energies resulting from the OPM are compared to Hartree-Fock and conventional DFT energies. Finally, we give some first OPM results for the correlation energies of the neon isoelectronic series.

## 1. Introduction

Density functional theory (DFT) is a well established approach for the description of many electron systems, comprising atoms, molecules, clusters and solids [1–4]. Its main advantage, as compared to other correlated many-body methods, like the configuration interaction or the multi-configuration Hartree-Fock (HF) scheme, is its particular computational efficiency. This is achieved by representing the nonclassical components of the electron-electron interaction as a functional of the density  $n$ , the so-called exchange-correlation ( $xc$ ) energy functional  $E_{xc}[n]$ . However, the exact functional dependence of  $E_{xc}$  on  $n$  is unknown to date, so that one has to resort to suitable approximations. While for a long time explicitly density-dependent variants of  $E_{xc}[n]$ , like the local density approximation (LDA) or the generalized gradient approximation (GGA) [5–8], were exclusively applied, now a new trend is emerging: In analogy to the kinetic energy functional  $T_s$  [9], also  $E_{xc}$  can be represented in terms of the Kohn-Sham (KS) orbitals, leading to the concept of orbital-dependent functionals, i.e. implicit density functionals [10–19].

An orbital-dependent representation has first been used for the exchange ( $x$ -only) energy functional  $E_x$  [20,5]. For  $E_x$  the Fock expression, written in terms of KS orbitals, represents the natural definition, as it exactly eliminates the self-interaction energy inherent in the classical Coulomb (Hartree) energy. Although the density dependence of this  $E_x[n]$  is unknown, it is nevertheless possible to obtain the corresponding multiplicative exchange potential  $v_x = \delta E_x / \delta n$  via the optimized potential method (OPM) [21]. Together with this representation of  $E_x$ , which is the simplest and most frequently applied orbital-dependent functional, various forms of the correlation energy

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$E_c = E_{xc} - E_x$  have been employed. On the one hand, LDA and GGA type correlation functionals have been used [14]. However, the success of the LDA (and, to a lesser extent, also the GGA) partially depends on an error cancellation between the exchange and correlation contributions, which is lost as soon as the exact  $E_x$  is used. On the other hand, the semiempirical orbital-dependent Colle-Salvetti functional [22] has been investigated [15]. Although the corresponding atomic correlation energies compare well [15] with the exact data extracted from experiment [23], the Colle-Salvetti correlation potential deviates substantially from the exact  $v_c = \delta E_c / \delta n$  [24] in the case of closed subshell atoms [25].

Based on a perturbation expansion using the KS Hamiltonian [26,27], recently a new systematic scheme for the derivation of orbital-dependent  $E_c$  has been proposed [12]. While this representation is exact in principle, an explicit evaluation requires the solution of a highly nonlinear equation, coupling  $E_{xc}$  and the corresponding  $v_{xc}$  [19]. For a rigorous treatment of this  $E_{xc}$  one thus has to resort to an expansion in powers of  $e^2$ , which allows to establish a recursive procedure for the evaluation of  $E_{xc}$  and the accompanying  $v_{xc}$ .

A fully relativistic extension of the scheme put forward in [12] has been introduced in [19], including the transverse electron-electron interaction (Breit + ...) and vacuum corrections. Restricting the discussion to the no-pair approximation [28] for simplicity, we here compare this perturbative approach to orbital-dependent  $E_{xc}$  to the relativistic variant of the adiabatic connection formalism [29], demonstrating that the latter allows for a direct extraction of an RPA-like orbital-dependent functional for  $E_{xc}$ . In addition, we provide some first numerical results for atomic  $E_c$ .

The paper is structured as follows. After a brief summary of relativistic DFT in Section 2.1, the nonlinear equation which determines the exact  $E_{xc}$  as a functional of the KS orbitals and eigenvalues is derived via KS perturbation theory in Sections 2.2, 2.3. It is explicitly shown that an expansion in powers of  $e^2$  allows to solve this nonlinear relation in a recursive manner. In Section 2.4 the adiabatic connection scheme is extended to inhomogeneous relativistic systems, extracting an RPA-like form for  $E_{xc}$ . The relativistic OPM (ROPM), which allows to evaluate the  $v_{xc}$  corresponding to orbital and eigenvalue dependent functionals is reviewed in Section 3. While the ROPM can be used straightforwardly with the recursive scheme for  $E_{xc}$ , its application to nonlinear forms of  $E_{xc}$  requires additional discussion. An approximate version of the ROPM, which allows to deal with such nonlinear forms is indicated. Finally, in Section 4 the orbital-dependent  $E_{xc}$  is specialized to the pure Coulomb interaction in order to facilitate comparison with standard many-body methods. The Coulomb form of the functionals also allows for a direct extraction of the nonrelativistic limit. A brief comparison of  $x$ -only ROPM results with relativistic HF (RHF) data for closed subshell atoms demonstrates the physical equivalence of the  $x$ -only ROPM with the RHF approach. Moreover, the corresponding LDA and GGA results illustrate the progress achieved by using the orbital-dependent exchange. First results for the correlation energies of the neon isoelectronic series (exact to the order  $e^4$ ) are also given in Section 4, and compared with conventional relativistic many-body perturbation theory (RMBPT) data [30]. It is found that for neutral neon the ROPM and RMBPT correlation energies differ by roughly 20%, while this disagreement vanishes with increasing  $Z$ .

The asymptotic  $-1/r$ -behaviour of the KS  $x$ -only potential, which leads to a Rydberg series of excited levels even for neutral atoms, is identified as the main source of this difference.

## 2. Systematic Approaches to the Exchange-Correlation Energy Functional

### 2.1. Relativistic density functional theory

The main feature of the relativistic generalization of the Hohenberg-Kohn theorem [31–35], as compared to its nonrelativistic counterpart [36], is the transition from the ground state density  $n$  as the basic DFT variable to the ground state four current  $j^\mu = (n, \mathbf{j})$ . Its crucial statement is: The ground state  $|\Phi\rangle$  of any stationary  $N$ -electron system is uniquely determined (up to gauge transformations) by the corresponding ground state four current

$$j^\mu(\mathbf{x}) = \langle \Phi | \hat{j}^\mu(x) | \Phi \rangle. \quad (2.1)$$

Consequently,  $|\Phi\rangle$  may be understood as a functional  $|\Phi[j^\mu]\rangle$  of the ground state four current. As an immediate result,  $j^\mu$  also determines all ground state expectation values, in particular the ground state energy  $E = E[j^\mu]$ .

Both  $E$  and  $j^\mu$  can in principle be simultaneously calculated using the variational property of the energy,  $\delta E[j]/\delta j = 0$  (the no-pair approximation is implied throughout this paper — the implications of an extension of the Hohenberg-Kohn theorem to the full QED problem including the negative energy states have been discussed in [34,35]). The energy minimization is most easily implemented by representing  $j^\mu$  via auxiliary single particle spinors,

$$j^\mu(\mathbf{x}) = \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \bar{\phi}_k(\mathbf{x}) \gamma^\mu \phi_k(\mathbf{x}) \quad (2.2)$$

(where it has been assumed that a noninteracting system with an external potential  $v_{KS}^\mu$  exists whose ground state four current is identical with the current of the actually interesting interacting system). The total energy  $E$  can then be decomposed as

$$E = T_s + \int d^3x j_\mu(\mathbf{x}) v_{ext}^\mu(\mathbf{x}) + E_H + E_{xc}, \quad (2.3)$$

where  $T_s$  represents the kinetic energy of the ‘auxiliary particles’,

$$T_s = \int d^3x \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \bar{\phi}_k(\mathbf{x}) [-ic\boldsymbol{\gamma} \cdot \nabla + mc^2] \phi_k(\mathbf{x}), \quad (2.4)$$

and  $v_{ext}^\mu$  denotes the given external potential (nuclei, applied fields). Furthermore,  $E_H$  is the ‘covariant’ Hartree energy,

$$\begin{aligned}
 E_H &= \frac{1}{2} \int d^3x \int d^4y D_{\mu\nu}^0(\mathbf{x} - \mathbf{y}, y^0) j^\mu(\mathbf{x}) j^\nu(\mathbf{y}) \\
 &= \frac{e^2}{2} \int d^3x \int d^3y \frac{j_\nu(\mathbf{x}) j^\nu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|},
 \end{aligned} \tag{2.5}$$

with  $D_{\mu\nu}^0$  being the noninteracting photon propagator (given precisely in (2.19)) and  $E_{xc}$  is the  $xc$ -energy, which is defined via Eq. (2.3). The energy minimization is now performed with respect to the orbitals, which leads to the single particle equations of relativistic DFT, introduced by Rajagopal, MacDonald and Vosko [32,33],

$$\{-i c \boldsymbol{\alpha} \cdot \nabla + \beta m c^2 + \alpha_\mu v_{KS}^\mu(\mathbf{x})\} \phi_k(\mathbf{x}) = \epsilon_k \phi_k(\mathbf{x}) \tag{2.6}$$

( $\alpha^\mu = \gamma^0 \gamma^\mu$ ). The corresponding effective single particle potential  $v_{KS}^\mu$  reflects the decomposition of the total energy,

$$v_{KS}^\mu(\mathbf{x}) = v_{ext}^\mu(\mathbf{x}) + v_H^\mu(\mathbf{x}) + v_{xc}^\mu(\mathbf{x}) \tag{2.7}$$

$$v_H^\mu(\mathbf{x}) = e^2 \int d^3y \frac{j^\mu(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|} \tag{2.8}$$

$$v_{xc}^\mu(\mathbf{x}) = \frac{\delta E_{xc}[j]}{\delta j_\mu(\mathbf{x})}, \tag{2.9}$$

with  $v_H^\mu$  being the Hartree potential and  $v_{xc}^\mu$  the  $xc$ -potential. Eqs. (2.2, 2.6–2.9) have to be solved selfconsistently, using some suitable approximation for the functional  $E_{xc}[j]$ .

While it is common practice to apply purely density-dependent approximations in (2.9), we here want to review the concept of orbital-dependent  $E_{xc}$ . Two different approaches to orbital-dependent  $E_{xc}$  have been introduced in the nonrelativistic context, both providing an exact representation of  $E_{xc}$ . To develop these approaches we now establish a connection between relativistic DFT and QED, which provides the most general framework for the discussion of the Coulomb many-body problem.

## 2.2. Field theoretical background

Starting from the standard QED Lagrangian, the Hamiltonian characterizing a system of interacting electrons in a static external potential  $v_{ext}^\mu(\mathbf{x})$  is readily obtained as the 00-component of the energy-momentum tensor (see e.g. [35]),

$$\hat{H} = \hat{H}_e(x^0) + \hat{H}_\gamma(x^0) + \hat{H}_{int}(x^0). \tag{2.10}$$

The individual components, the electronic Hamiltonian  $\hat{H}_e$ , the free photon Hamiltonian  $\hat{H}_\gamma$  and the electron-photon coupling Hamiltonian  $\hat{H}_{int}$  are given by [37]

$$\hat{H}_e(x^0) = \int d^3x \hat{\psi}(x) (-ic\boldsymbol{\gamma} \cdot \nabla + mc^2 + \gamma_\mu v_{ext}^\mu(\mathbf{x})) \hat{\psi}(x) \quad (2.11)$$

$$\hat{H}_\gamma(x^0) = -\frac{1}{8\pi} \int d^3x \{ \partial^0 \hat{A}_\nu(x) \partial^0 \hat{A}^\nu(x) + \nabla \hat{A}_\nu(x) \cdot \nabla \hat{A}^\nu(x) \} \quad (2.12)$$

$$\hat{H}_{int}(x^0) = e \int d^3x \hat{j}^\mu(x) \hat{A}_\mu(x). \quad (2.13)$$

Besides the nuclear attraction,  $v_{ext}^\mu(\mathbf{x})$  could also include additional external fields, if present.  $\hat{\psi}(x)$  denotes the fermion field operator of the interacting, inhomogeneous system characterized by  $\hat{H}$ ,  $\hat{j}^\mu(x)$  is the corresponding fermion four current operator,

$$\hat{j}^\mu(x) = \hat{\bar{\psi}}(x) \gamma^\mu \hat{\psi}(x) \quad (2.14)$$

and  $\hat{A}_\mu(x)$  represents the field operator of the photons for which the covariant quantization scheme (Feynman gauge) has been used.

Following the common approach in relativistic field theory, which aims at a manifestly covariant representation of the dynamics inherent in the field operators, so far all quantities have been introduced in the Heisenberg picture. To develop the framework of relativistic DFT, however, it is common practice to transform to the Schrödinger picture, so that the relativistic theory can be formulated in close analogy to its nonrelativistic limit. As usual we choose the two pictures to coincide at  $x^0 = 0$ . Once the field operators in the Schrödinger-picture have been identified via  $\hat{\psi}_S(\mathbf{x}) = \hat{\psi}(\mathbf{x}, x^0 = 0)$ , etc, the Hamiltonians  $\hat{H}_{e,S}$ ,  $\hat{H}_{\gamma,S}$  and  $\hat{H}_{int,S}$  are immediately obtained in terms of the Schrödinger-picture field operators.

Let us for the moment assume that the KS-potential (2.7) is known. This potential then allows to define a noninteracting KS Hamiltonian

$$\hat{H}_{KS} = \int d^3x \hat{\bar{\psi}}_S(\mathbf{x}) (-ic\boldsymbol{\gamma} \cdot \nabla + mc^2) \hat{\psi}_S(\mathbf{x}) + \int d^3x \hat{j}_{S,\mu}(\mathbf{x}) v_{KS}^\mu(\mathbf{x}) + \hat{H}_{\gamma,S}, \quad (2.15)$$

which provides a decomposition of  $\hat{H}$ ,

$$\hat{H} = \hat{H}_{KS} + \hat{H}_{1,S}, \quad (2.16)$$

which is particularly suitable for our present purpose. We will later come back to the point how to calculate the selfconsistent  $v_{KS}^\mu$ . As electrons and photons do not interact in  $\hat{H}_{KS}$ , the ground state  $|\Phi_{KS}\rangle$  of  $\hat{H}_{KS}$ ,

$$\hat{H}_{KS} |\Phi_{KS}\rangle = E_{KS} |\Phi_{KS}\rangle, \quad (2.17)$$

can be factorized into a product of the photon vacuum  $|0_\gamma\rangle$  (no free photons are present in the ground state) and an electronic ground state  $|\Phi_{KS,e}\rangle$ ,

$$|\Phi_{KS}\rangle = |\Phi_{KS,e}\rangle \times |0_\gamma\rangle; \langle 0_\gamma | \hat{A}_0^\mu(x) | 0_\gamma \rangle = 0, \quad (2.18)$$

where  $\hat{A}_0^\mu(x)$  denotes the free photon field operator. As a consequence, standard vacuum QED results can be used for the photon sector of the noninteracting problem defined by  $\hat{H}_{KS}$ , as e.g. the free photon propagator (Feynman gauge)

$$\begin{aligned} D^{0,\mu\nu}(x-y) &= -i \frac{e^2}{c} \langle 0_\gamma | T \hat{A}_0^\mu(x) \hat{A}_0^\nu(y) | 0_\gamma \rangle \\ &= g^{\mu\nu} \int \frac{d^4 q}{(2\pi)^4} e^{-iq(x-y)} \frac{-4\pi e^2}{q^2 + i\eta}. \end{aligned} \quad (2.19)$$

In the electronic sector the presence of the potential  $v_{KS}^\mu$  leads to an inhomogeneous reference system. Within the no-pair approximation,

$$\hat{\psi}_{S,np}(\mathbf{x}) = \mathcal{L}_+ \hat{\psi}_S(\mathbf{x}) \mathcal{L}_+, \quad (2.20)$$

where  $\mathcal{L}_+$  is the projection operator onto the space spanned by the positive energy eigenstates  $\phi_k$  of  $\hat{H}_{KS}$  [28, 38], the noninteracting field operators are given by

$$\hat{\psi}_{0,np}(x) = e^{i\hat{H}_{KS}x^0/c} \hat{\psi}_{S,np}(\mathbf{x}) e^{-i\hat{H}_{KS}x^0/c} = \sum_{-mc^2 < \epsilon_k} \hat{b}_k \phi_k(\mathbf{x}) e^{-i\epsilon_k x^0/c} \quad (2.21)$$

$$\hat{\psi}_{0,np}^\dagger(x) = \sum_{-mc^2 < \epsilon_k} \hat{b}_k^\dagger \phi_k^\dagger(\mathbf{x}) e^{i\epsilon_k x^0/c} \quad (2.22)$$

(As all quantities discussed in this publication are understood within the no-pair approximation, we will omit the index  $np$  in the following for brevity). In Eqs. (2.21, 2.22)  $\hat{b}_k$  and  $\hat{b}_k^\dagger$  are the annihilation and creation operators for positive energy KS states, which allow to write the electronic ground state as

$$|\Phi_{KS,e}\rangle = \prod_{-mc^2 < \epsilon_k \leq \epsilon_F} \hat{b}_k^\dagger |0_e\rangle, \quad (2.23)$$

where the electronic single particle states have been assumed to be filled up to the Fermi level  $\epsilon_F$  (both the  $\hat{\psi}_0^{(\dagger)}$  and the  $\hat{b}_k^{(\dagger)}$  satisfy the standard commutation relations, of course). The corresponding electron propagator is given by

$$G^0(x, y) \equiv G^0(\mathbf{x}, \mathbf{y}, x^0 - y^0) = -i \langle \Phi_{KS,e} | T \hat{\psi}_0(x) \hat{\psi}_0(y) | \Phi_{KS,e} \rangle \quad (2.24)$$

$$\begin{aligned} &= -i \Theta(x^0 - y^0) \sum_{\epsilon_F < \epsilon_k} \phi_k(\mathbf{x}) \bar{\phi}_k(\mathbf{y}) e^{-i\epsilon_k(x^0 - y^0)/c} \\ &\quad + i \Theta(y^0 - x^0) \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \phi_k(\mathbf{x}) \bar{\phi}_k(\mathbf{y}) e^{-i\epsilon_k(x^0 - y^0)/c}. \end{aligned} \quad (2.25)$$

Using (2.14, 2.21–2.23) the ground state four current

$$j^\mu(\mathbf{x}) = \langle \Phi_{KS} | \hat{j}^\mu(\mathbf{x}) | \Phi_{KS} \rangle, \quad (2.26)$$

is obtained in the form introduced in Eq. (2.2) and the ground state energy reads

$$E_{KS} = T_s + \int d^3x j_\mu(\mathbf{x}) v_{KS}^\mu(\mathbf{x}). \quad (2.27)$$

In fact, the field theoretical formulation of the KS problem via Eqs. (2.15–2.27) in the

no-pair approximation is the actual origin of the forms (2.2, 2.4) for the KS four current and  $T_s$ .

In the following the KS Hamiltonian is used to analyze the total energy  $E$  of the ground state  $|\Phi\rangle$  of  $\hat{H}$ ,

$$\hat{H}|\Phi\rangle = E|\Phi\rangle, \quad (2.28)$$

using a perturbation expansion in terms of  $\hat{H} - \hat{H}_{KS}$ . For expansions of this type different techniques have been used in the literature. On the one hand, in the framework of QED usually the level shift formula of Gell-Mann and Low [39] in the symmetric form of Sucher [40] is applied (see e.g. [41–44]). In the context of nonrelativistic DFT, on the other hand, two versions of a coupling constant integration have been utilized for such purposes. While the so-called adiabatic connection [29,45] has been particularly useful for the analysis of  $E_{xc}$  [46–48] in the context of explicit density functionals, the second scheme [26,27] allows a systematic extraction of orbital-dependent forms for  $E_{xc}$ , i.e implicit density functionals, so that we first discuss the extension of this latter variant to the relativistic domain.

### 2.3. Perturbation theory on Kohn-Sham basis

In order to obtain a formula for the energy difference between the complete ground state energy  $E$  and the noninteracting energy  $E_{KS}$ , and thus for  $E_{xc}$ , the interaction Hamiltonian  $\hat{H}_1 = \hat{H} - \hat{H}_{KS}$  is supplemented by a dimensionless coupling strength parameter  $g$  in such a way,

$$\hat{H}(g) = \hat{H}_{KS} + \hat{H}_{1,S}(g) \quad (2.29)$$

$$\hat{H}_1(x^0) = \int d^3x \hat{j}_\mu(x) [g^{1/2} e \hat{A}^\mu(x) - g v_{Hxc}^\mu(\mathbf{x})] \quad (2.30)$$

$$v_{Hxc}^\mu(\mathbf{x}) \equiv v_{KS}^\mu(\mathbf{x}) - v_{ext}^\mu(\mathbf{x}) = v_H^\mu(\mathbf{x}) + v_{xc}^\mu(\mathbf{x}), \quad (2.31)$$

that the scaling of the two contributions to  $\hat{H}_1$  with  $g$  reflects their dependence on the actual coupling constant  $e^2$  (at least to lowest order of  $v_{Hxc}$  — see below). The original Hamiltonian (2.10) is then obtained from (2.29) for  $g = 1$ . The desired expression for the energy shift induced by the interaction is obtained by first differentiating the  $g$ -dependent ground state energy

$$E(g) = \langle \Phi(g) | \hat{H}(g) | \Phi(g) \rangle \quad (2.32)$$

with respect to the coupling parameter. One finds

$$\frac{\partial}{\partial g} E(g) = \int d^4x \delta(x^0) \langle \Phi(g) | \hat{j}_\mu(x) \left[ \frac{e}{2g^{1/2}} \hat{A}^\mu(x) - v_{Hxc}^\mu(\mathbf{x}) \right] | \Phi(g) \rangle, \quad (2.33)$$

where the normalization of  $|\Phi(g)\rangle$ ,

$$\langle \Phi(g) | \Phi(g) \rangle = 1, \quad (2.34)$$

has been used. In the second step integration over  $g$  leads to

$$\begin{aligned}
 E(1) - E(0) &= E - E_{KS} \equiv E_1 \\
 &= \int_0^1 dg \int d^4x \delta(x^0) \langle \Phi(g) | \hat{j}_\mu(x) \left[ \frac{e}{2g^{1/2}} \hat{A}^\mu(x) - v_{Hxc}^\mu(\mathbf{x}) \right] | \Phi(g) \rangle. \quad (2.35)
 \end{aligned}$$

Further evaluation of Eq. (2.35) requires an expression connecting  $|\Phi(g)\rangle$  (assumed to be nondegenerate) with  $|\Phi_{KS}\rangle$  (also assumed to be nondegenerate). This link is established via the interaction-picture time-evolution operator  $\hat{U}_{I,\epsilon}$ , i.e. by an adiabatic switching of  $\hat{H}_1$ ,

$$|\Phi\rangle = A \lim_{\epsilon \rightarrow 0} \frac{\hat{U}_{I,\epsilon}(0, \mp\infty) |\Phi_{KS}\rangle}{\langle \Phi_{KS} | \hat{U}_{I,\epsilon}(0, \mp\infty) | \Phi_{KS} \rangle} \quad (2.36)$$

$$A = \lim_{\epsilon_1, \epsilon_2 \rightarrow 0} \left[ \frac{\langle \Phi_{KS} | \hat{U}_{I,\epsilon_1}(+\infty, 0) | \Phi_{KS} \rangle \langle \Phi_{KS} | \hat{U}_{I,\epsilon_2}(0, -\infty) | \Phi_{KS} \rangle}{\langle \Phi_{KS} | \hat{U}_{I,\epsilon_1}(+\infty, 0) \hat{U}_{I,\epsilon_1}(0, -\infty) | \Phi_{KS} \rangle} \right]^{1/2} \quad (2.37)$$

$$\begin{aligned}
 \hat{U}_{I,\epsilon}(t, t') &= \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{t'}^t dt_1 \cdots \int_{t'}^t dt_n \exp[-\epsilon(|t_1| + \cdots + |t_n|)] T[\hat{H}_{1,I}(t_1) \cdots \hat{H}_{1,I}(t_n)] \\
 &\quad (2.38)
 \end{aligned}$$

$$\hat{H}_{1,I}(x^0) = e^{i\hat{H}_{KS}x^0/c} \hat{H}_{1,s} e^{-i\hat{H}_{KS}x^0/c} = \int d^3x \hat{j}_{0,\mu}(x) [g^{1/2} e \hat{A}_0^\mu(x) - g v_{Hxc}^\mu(\mathbf{x})] \quad (2.36)$$

(for brevity, the  $g$ -dependence of the various operators and states involved is no longer noted explicitly). Together with the normalization of  $\langle \Phi_{KS} | \Phi_{KS} \rangle = 1$  the factor (2.37) ensures the validity of (2.34) for all  $g$ . Insertion of (2.36) into (2.35) and use of the additivity of the time-evolution operator gives

$$\begin{aligned}
 E_1 &= \lim_{\epsilon \rightarrow 0} \int_0^1 dg \int d^4x \delta(x^0) \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n e^{-\epsilon(|t_1| + \cdots + |t_n|)} \\
 &\quad \times \frac{\langle \Phi_{KS} | T \hat{j}_{0,\mu}(x) [(e/2g^{1/2}) \hat{A}^\mu(x) - v_{Hxc}^\mu(\mathbf{x})] \hat{H}_{1,I}(t_1) \cdots \hat{H}_{1,I}(t_n) | \Phi_{KS} \rangle}{\langle \Phi_{KS} | \hat{U}_{I,\epsilon}(+\infty, -\infty) | \Phi_{KS} \rangle}. \quad (2.40)
 \end{aligned}$$

Eq. (2.40) directly leads to a perturbative expansion of  $E_1$  in powers of  $e$ ,

$$\begin{aligned}
 E_1 &= \lim_{\epsilon \rightarrow 0} \int_0^1 dg \sum_{n=0}^{\infty} \frac{(-i)^n}{n! c^n} \sum_{k=0}^n \binom{n}{k} g^{n-k/2} \int d^4x \delta(x^0) \int d^4x_1 \cdots \int d^4x_n e^{-\epsilon(|x_1^0| + \cdots + |x_n^0|)} \\
 &\quad \times \langle \Phi_{KS,e} | T \hat{j}_0^\mu(x) \hat{j}_0^{\mu_1}(x_1) \cdots \hat{j}_0^{\mu_n}(x_n) | \Phi_{KS,e} \rangle_c (-1)^{n-k} v_{Hxc,\mu_{k+1}}(\mathbf{x}_{k+1}) \cdots v_{Hxc,\mu_n}(\mathbf{x}_n) \\
 &\quad \times e^k \left\{ \frac{e}{2g^{1/2}} \langle 0_\gamma | T \hat{A}_{0,\mu}(x) \hat{A}_{0,\mu_1}(x_1) \cdots \hat{A}_{0,\mu_k}(x_k) | 0_\gamma \rangle \right. \\
 &\quad \left. - v_{Hxc,\mu}(\mathbf{x}) \langle 0_\gamma | T \hat{A}_{0,\mu_1}(x_1) \cdots \hat{A}_{0,\mu_k}(x_k) | 0_\gamma \rangle \right\}, \quad (2.41)
 \end{aligned}$$

where the index  $c$  indicates that only those diagrammatic contributions are to be included in which all vertices  $x_1 \cdots x_n$  are connected to the vertex  $x$  (the remaining terms are exactly cancelled by the denominator of (2.40)). Eliminating all photon operators in favor of the photon propagator (2.19), the expansion (2.41) can be directly ordered in powers of  $e^2$ . Recalling that due to (2.18) the vacuum expectation value of an odd number of  $\hat{A}_0$  vanishes, only terms with an even number of photon operators contribute. In the latter case all possible contractions, i.e. permutations of the  $\hat{A}_0$ , are obtained by

$$\begin{aligned} & \langle 0_\gamma | T \hat{A}_0^{\mu_1}(x_1) \cdots \hat{A}_0^{\mu_{2n}}(x_{2n}) | 0_\gamma \rangle \\ &= \sum_{k=2}^{2n} \langle 0_\gamma | T \hat{A}_0^{\mu_1}(x_1) \hat{A}_0^{\mu_k}(x_k) | 0_\gamma \rangle \langle 0_\gamma | T \hat{A}_0^{\mu_2}(x_2) \cdots \hat{A}_0^{\mu_k}(x_k) \cdots \hat{A}_0^{\mu_{2n}}(x_{2n}) | 0_\gamma \rangle \end{aligned} \quad (2.42)$$

(here  $\hat{A}_0^{\mu_k}(x_k)$  indicates that this operator has to be dropped from the series  $k = 2, \dots, 2n$ ). From Eq. (2.18) it therefore follows that  $k$  must be odd in the first term inside the curly brackets in (2.41) and even in the second. The interchange of the summation order of  $k$  and  $n$  now allows to separate the contributions with even from those with odd  $k$ . Subsequently the photon vacuum expectation values are evaluated using (2.42). Taking into account the multiplicity originating from the number of possible contractions of the  $\hat{A}_0$  (Wick's theorem) this leads to

$$\begin{aligned} E_1 &= \lim_{c \rightarrow 0} \int_0^1 dg \sum_{l=0}^{\infty} \frac{(ig)^l}{l! c^l} \sum_{k=0}^l \binom{l}{k} \left(-\frac{1}{2}\right)^k \int d^4 x \delta(x^0) \int d^4 x_1 \cdots \int d^4 x_{l+k} e^{-c(|x_1^0| + \cdots + |x_{l+k}^0|)} \\ &\quad \times D_{\mu_1 \mu_2}^0(x_1 - x_2) \cdots D_{\mu_{2k-1} \mu_{2k}}^0(x_{2k-1} - x_{2k}) v_{Hxc, \mu_{2k+1}}(\mathbf{x}_{2k+1}) \cdots v_{Hxc, \mu_{l+k}}(\mathbf{x}_{l+k}) \\ &\quad \times \left\{ \frac{1}{2} \int d^4 y e^{-c|y^0|} D_{\mu\nu}^0(x - y) \langle \Phi_{KS,e} | T \hat{j}_0^\mu(x) \hat{j}_0^\nu(y) \hat{j}_0^{\mu_1}(x_1) \cdots \hat{j}_0^{\mu_{l+k}}(x_{l+k}) | \Phi_{KS,e} \rangle_c \right. \\ &\quad \left. - v_{Hxc, \mu}(\mathbf{x}) \langle \Phi_{KS,e} | T \hat{j}_0^\mu(x) \hat{j}_0^{\mu_1}(x_1) \cdots \hat{j}_0^{\mu_{l+k}}(x_{l+k}) | \Phi_{KS,e} \rangle_c \right\}. \end{aligned} \quad (2.43)$$

Finally, this result can be given a more compact form, if the binomial relation is used to eliminate the  $k$ -summation. The  $xc$ -contribution is extracted from  $E_1$  via (2.3, 2.27, 2.35). Introducing the interaction operator

$$\begin{aligned} \hat{W}(x^0) &= \frac{1}{2} \int d^3 x \int d^4 y e^{-c(|x^0| + |y^0|)} \hat{j}_0^\mu(x) D_{\mu\nu}^0(x - y) \hat{j}_0^\nu(y) \\ &\quad - \int d^3 x e^{-c|x^0|} \{ v_{H, \mu}(\mathbf{x}) + v_{xc, \mu}(\mathbf{x}) \} \hat{j}_0^\mu(x), \end{aligned} \quad (2.44)$$

the final result for  $E_{xc}$  can be written as

$$\begin{aligned}
E_{xc} &= \frac{1}{2} \int d^4x \delta(x^0) \int d^4y e^{-\epsilon|y^0|} D_{\mu\nu}^0(x-y) \{ \langle \Phi_{KS} | T \hat{j}_0^\mu(x) \hat{j}_0^\nu(y) | \Phi_{KS} \rangle - j^\mu(x) j^\nu(y) \} \\
&+ \lim_{\epsilon \rightarrow 0} \sum_{n=1}^{\infty} \frac{(-i)^n}{(n+1)!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n \langle \Phi_{KS} | T \hat{W}(0) \hat{W}(t_1) \cdots \hat{W}(t_n) | \Phi_{KS} \rangle_{\epsilon},
\end{aligned} \tag{2.45}$$

with the additional convention that, in analogy to the time-evolution operator, the time-ordering in (2.45) also applies inside (2.44), i.e. before performing the time integrations in the individual  $\hat{W}$  the overall time-ordering of (2.45) has to be established.

Without going into details we just remark that Eq. (2.45) can be further simplified by applying Wick's theorem to the electronic sector, utilizing the KS propagator (2.25). Taking into account the explicit form (2.8) for  $v_{xc}^\mu$  it is then possible to eliminate a further class of diagrammatic contributions (the interested reader is referred to [19] for details). Eq. (2.45), which provides an exact representation of  $E_{xc}$  in terms of the KS orbitals, the KS eigenvalues and the  $xc$ -potential,  $E_{xc}[\phi_k^{(\dagger)}, \epsilon_k, v_{xc}^\mu]$ , is the central result of this Section. Note that the  $\phi_k^{(\dagger)}$ ,  $\epsilon_k$  and  $v_{xc}^\mu$  are implicit functionals of  $j^\mu$ , so that the same is true for  $E_{xc}$ .

However, Eq. (2.45) is not suitable for a direct evaluation of the  $xc$ -energy. In fact, as  $v_{xc}^\mu = \delta E_{xc} / \delta j_\mu$  the  $xc$ -energy appears on both sides of Eq. (2.45), i.e. Eq. (2.45) represents a highly nonlinear relation for  $E_{xc}$ . This highly nonlinear character can be resolved by an expansion in powers of  $e^2$ ,

$$E_{xc} = \sum_{i=1}^{\infty} e^{2i} E_{xc}^{(i)}, \quad v_{xc}^\mu = \sum_{i=1}^{\infty} e^{2i} v_{xc}^{\mu,(i)}. \tag{2.46}$$

After insertion of Eq. (2.46) into (2.45) one notices that the lowest order contribution in  $e^2$ , the exchange energy  $E_x = e^2 E_{xc}^{(1)}$ , does not depend on  $v_{xc}^\mu$ . Explicitly one obtains

$$E_x = -\frac{e^2}{2} \int d^3r \int d^3r' \sum_{-mc^2 < \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\cos(\omega_{kl} |\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \phi_k^\dagger(\mathbf{r}) \alpha_\mu \phi_l(\mathbf{r}) \phi_l^\dagger(\mathbf{r}') \alpha^\mu \phi_k(\mathbf{r}'), \tag{2.47}$$

where  $\omega_{kl}$  represents the KS single particle transition frequencies

$$\omega_{kl} = |\epsilon_k - \epsilon_l|/c. \tag{2.48}$$

In (2.47) we have again chosen to work in Feynman gauge, which is technically simplest to handle. This choice does not introduce any gauge dependence, as demonstrated in [19]. Thus  $E_x$  is a well-defined functional of the  $\phi_k^{(\dagger)}$  and  $\epsilon_k$ . The corresponding exchange potential  $v_x^\mu$  can be evaluated using the ROPM in the order  $e^2$  (see Section 3).

This then unambiguously defines the  $e^4$ -contribution to  $E_{xc}$ , as only  $v_x^\mu = e^2 v_{xc}^{\mu,(1)}$  enters in (2.45) in this order,

$$\begin{aligned}
 E_c^{(2)} = & \frac{i}{2c} \lim_{\epsilon \rightarrow 0} \int d^4 x \delta(x^0) \int d^4 y e^{-\epsilon|y^0|} \\
 & \times \left\{ -v_{x,\mu}(\mathbf{x}) v_{x,\nu}(\mathbf{y}) \text{tr}[\gamma^\mu G^0(x, y) \gamma^\nu G_0(y, x)] \right. \\
 & + i \int d^4 z e^{-\epsilon|z^0|} [D_{\mu\rho}^0(x-z) v_{x,\nu}(\mathbf{y}) + D_{\nu\rho}^0(y-z) v_{x,\mu}(\mathbf{x})] \\
 & \times \text{tr}[\gamma^\mu G_0(x, y) \gamma^\nu G_0(y, z) \gamma^\rho G^0(z, x)] \\
 & - \frac{1}{2} \int d^4 z \int d^4 u e^{-\epsilon(|z^0|+|u^0|)} D_{\mu\nu}^0(x-z) D_{\rho\lambda}^0(y-u) \\
 & \times \{ \text{tr}[\gamma^\mu G^0(x, y) \gamma^\rho G^0(y, x)] \text{tr}[\gamma^\nu G^0(z, u) \gamma^\lambda G^0(u, z)] \\
 & - 2 \text{tr}[\gamma^\mu G^0(x, z) \gamma^\nu G^0(z, u) \gamma^\lambda G^0(u, y) \gamma^\rho G^0(y, x)] \\
 & \left. - \text{tr}[\gamma^\mu G^0(x, y) \gamma^\rho G^0(y, z) \gamma^\nu G^0(z, u) \gamma^\lambda G^0(u, x)] \right\}, \quad (2.49)
 \end{aligned}$$

so that the corresponding potential  $v_c^{(2)}$  can again be calculated by the ROPM. Generalizing this procedure to all orders, it is obvious, that  $E_{xc}^{(n)}$  only depends on those  $v_{xc}^{\mu,(i)}$  with  $i < n$ . Therefore a recursive definition of  $E_{xc}$  in terms of the  $\phi_k^{(\dagger)}$  and  $\epsilon_k$  is established.

We have thus found a systematic perturbative approach to orbital-dependent representations of  $E_{xc}$ . In many physical situations, however, the resummation of certain classes of diagrammatic contributions is required, or at least very helpful. The most simple resummation of this type, the RPA, can be derived most easily within the framework of the adiabatic connection scheme, which is extended to inhomogeneous relativistic systems in the next Section.

#### 2.4. Adiabatic connection formula

The relativistic adiabatic connection formula is based on a modified Hamiltonian  $\hat{H}(g)$  in which not only the electron-photon coupling strength is multiplied by the dimensionless scaling parameter  $g$  but also a  $g$ -dependent, multiplicative, external potential is introduced,

$$\hat{H}(g) = \hat{H}_{0,S}(g) + g \hat{H}_{int,S} \quad (2.50)$$

$$\begin{aligned}
 \hat{H}_{0,S}(g) = & \int d^3 x \hat{\psi}_S(\mathbf{x}) (-ic\boldsymbol{\gamma} \cdot \nabla + mc^2) \hat{\psi}_S(\mathbf{x}) \\
 & + \int d^3 x \hat{j}_{S,\mu}(\mathbf{x}) v_g^\mu(\mathbf{x}) + \hat{H}_\gamma(x^0 = 0). \quad (2.51)
 \end{aligned}$$

The physically relevant limit (2.10) is obtained from Eq. (2.50) for  $g = 1$ , for which  $v_g^\mu$  coincides with the actual external potential,

$$v_{g=1}^\mu(\mathbf{x}) \equiv v_{ext}^\mu(\mathbf{x}). \quad (2.52)$$

Moreover, assuming noninteracting  $v$ -representability [2],  $v_g^\mu$  is chosen so, that for all  $g < 1$  the corresponding ground state  $|\Phi(g)\rangle$  yields the exact interacting ground state four current

$$j^\mu(\mathbf{x}) = \langle \Phi(g) | \hat{j}^\mu(x) | \Phi(g) \rangle, \quad \forall g \leq 1. \quad (2.53)$$

Consequently, while for vanishing  $g$  the noninteracting Hamiltonian  $\hat{H}_{0,S}(g)$  is identical with the KS Hamiltonian,

$$v_{g=0}^\mu(\mathbf{x}) = v_{KS}^\mu(\mathbf{x}), \quad (2.54)$$

the noninteracting ground state  $|\Phi_0\rangle$  depends on  $g$ ,

$$\hat{H}_{0,S}(g) |\Phi_0(g)\rangle = E_0(g) |\Phi_0(g)\rangle, \quad (2.55)$$

in contrast to the scheme of Section 2.3.

With this construction of the noninteracting reference system one finds for the  $g$ -dependent interacting ground state energy  $E(g)$ ,

$$\frac{\partial}{\partial g} E(g) = \langle \Phi(g) | \hat{H}_{int,S} | \Phi(g) \rangle + \int d^3x j_\mu(\mathbf{x}) \frac{\partial}{\partial g} v_g^\mu(\mathbf{x}), \quad (2.56)$$

and thus by integration over  $g$  and subsequent insertion of (2.27, 2.52, 2.54)

$$E = T_s + \int d^3x j_\mu(\mathbf{x}) v_{ext}^\mu(\mathbf{x}) + E_{int}, \quad (2.57)$$

$$E_{int} = \int_0^1 dg \langle \Phi(g) | \hat{H}_{int,S} | \Phi(g) \rangle. \quad (2.58)$$

At this point one can apply the standard techniques of many-body theory introduced in the previous subsection to obtain (2.40) with  $\hat{H}_1$  and  $|\Phi_{KS}\rangle$  being replaced by  $g\hat{H}_{int}$  and  $|\Phi_0\rangle$ , respectively. Using (2.42) one can rewrite  $E_{int}$  as

$$\begin{aligned} E_{int} &= \lim_{\epsilon \rightarrow 0} \int_0^1 dg g \int d^4x \delta(x^0) \int d^4y e^{-\epsilon|y^0|} D_{\mu\nu}^0(x-y) \\ &\quad \times \sum_{n=1}^{\infty} \frac{(-ig)^{n-1}}{(n-1)!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_{n-1} e^{-\epsilon(|t_1| + \cdots + |t_{n-1}|)} \\ &\quad \times \frac{\langle \Phi_0 | T \hat{j}_0^\mu(x) \hat{j}_0^\nu(y) \hat{H}_{int,I}(t_1) \cdots \hat{H}_{int,I}(t_{n-1}) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon}(+\infty, -\infty) | \Phi_0 \rangle} \end{aligned} \quad (2.59)$$

(the relation (2.42) leads to  $n$  identical contributions which can be added up after relabelling the integration variables). Distinguishing the two possible time-orderings of  $x^0$  and  $y^0$  one can reorder (2.59) as

$$\begin{aligned}
E_{int} &= \lim_{\epsilon \rightarrow 0} \int_0^1 dg g \int d^4 x \delta(x^0) \int d^4 y e^{-\epsilon|u^0|} D_{\mu\nu}^0(x-y) \\
&\times \left\{ \Theta(x^0 - y^0) \frac{\langle \Phi_0 | \hat{U}_{I,\epsilon}(+\infty, x^0) \hat{j}_0^\mu(x) \hat{U}_{I,\epsilon}(x^0, y^0) \hat{j}_0^\nu(y) \hat{U}_{I,\epsilon}(y^0, -\infty) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon}(+\infty, -\infty) | \Phi_0 \rangle} \right. \\
&\left. + \Theta(y^0 - x^0) \frac{\langle \Phi_0 | \hat{U}_{I,\epsilon}(+\infty, y^0) \hat{j}_0^\nu(y) \hat{U}_{I,\epsilon}(y^0, x^0) \hat{j}_0^\mu(x) \hat{U}_{I,\epsilon}(x^0, -\infty) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{U}_{I,\epsilon}(+\infty, -\infty) | \Phi_0 \rangle} \right\}.
\end{aligned}$$

Reintroducing the interacting current operator one then obtains

$$E_{int} = \int_0^1 dg g \int d^4 x \delta(x^0) \int d^4 y D_{\mu\nu}^0(x-y) \langle \Phi(g) | T \hat{j}^\mu(x) \hat{j}^\nu(y) | \Phi(g) \rangle, \quad (2.60)$$

where it has been assumed that the limit  $\epsilon \rightarrow 0$  is only relevant for the construction of the Heisenberg ground state  $|\Phi(g)\rangle$ . With the standard definition of the time-ordered current-current response function of the interacting system,

$$\chi_g^{\mu\nu}(x, y) = \chi_g^{\mu\nu}(\mathbf{x}, \mathbf{y}, x^0 - y^0) = -i[\langle \Phi(g) | T \hat{j}^\mu(x) \hat{j}^\nu(y) | \Phi(g) \rangle - j^\mu(\mathbf{x}) j^\nu(\mathbf{y})], \quad (2.61)$$

one finally obtains

$$E_{xc} = E_{int} - E_H = \frac{i}{2} \int_0^1 dg^2 \int d^3 x \int d^4 y D_{\mu\nu}^0(x-y) \chi_g^{\mu\nu}(x, y). \quad (2.62)$$

Eq. (2.62) is the relativistic extension of the adiabatic connection formula introduced by Gunnarsson and Lundqvist [49] and Langreth and Perdew [50]. The latter has proven to be very useful both for the analysis of  $E_{xc}$  [46–48] and for the derivation of approximations in the context of explicit density functionals [5]. This is due to the fact that the construction of explicitly density-dependent forms for  $E_{xc}$  is usually based on the homogeneous electron gas (HEG), either directly in the case of the LDA, or indirectly via the response of the HEG to a weak perturbation for gradient corrected functionals. While in the former situation Eq. (2.62) directly provides a representation of  $E_{xc}$  in terms of the linear HEG response function, in the latter case an expansion of  $\chi_g^{\mu\nu}$  in powers of  $v_g^\mu$  is required, resulting in an expression for  $E_{xc}$  which, in general, also depends on the nonlinear response functions of the HEG. Using standard many-body techniques for the HEG response functions, these ingredients of (2.62) only depend on the density via the Fermi momentum  $k_F = (3\pi^2 n_0)^{1/3}$  of the corresponding noninteracting HEG, which is independent of  $g$ . The coupling constant integration in (2.62) can thus be performed either directly in the case of the LDA or after a suitable discussion of the  $g$ -dependence of  $v_g^\mu$  [5].

In the case of arbitrary, inhomogeneous systems the situation is somewhat more complicated, so that for simplicity we restrict the discussion to the RPA, defined via

$$\chi_{g,RPA}^{\mu\nu}(x, y) = \chi_0^{\mu\nu}(x, y) + \frac{g^2}{c} \int d^4 z d^4 u \chi_0^{\mu\rho}(x, z) D_{\rho\kappa}^0(z-u) \chi_{g,RPA}^{\kappa\nu}(u, y), \quad (2.63)$$

as usual. Its basic ingredient is the noninteracting response function  $\chi_0^{\mu\nu}$  obtained from (2.61) in the limit  $g = 0$ , i.e. the KS response function

$$\begin{aligned}\chi_0^{\mu\nu}(x, y) &= -i[\langle \Phi_{KS} | T \hat{j}_0^\mu(x) \hat{j}_0^\nu(y) | \Phi_{KS} \rangle - j^\mu(\mathbf{x}) j^\nu(\mathbf{y})] \\ &= -i \text{Tr}[\gamma^\mu G^0(x, y) \gamma^\nu G^0(y, x)] \\ &= \chi_0^{\mu\nu}(\mathbf{x}, \mathbf{y}, x^0 - y^0).\end{aligned}\tag{2.64}$$

For all  $g$ , however, the  $g$ -independence of the corresponding  $j^\mu$  (defining  $v_g^\mu$ ) implies that the KS system corresponding to the interacting system with coupling strength  $g < 1$  is identical with the KS system corresponding to the fully interacting system with  $g = 1$ . As a consequence the KS single particle orbitals and thus  $\chi_0^{\mu\nu}$  are independent of  $g$ . Taking into account the  $g$ -dependence of the electron-electron interaction one finds

$$\begin{aligned}E_{xc}^{RPA} &= \frac{i}{2} \sum_{n=0}^{\infty} \frac{1}{n} \int d^4 x_1 \int d^4 y_1 \cdots \int d^4 x_n \int d^4 y_n \delta x_1^0 \\ &\quad \times D_{\mu_1 \nu_1}^0(x_1 - y_1) \chi_0^{\nu_1 \mu_2}(y_1, x_2) \cdots D_{\mu_n \nu_n}^0(x_n - y_n) \chi_0^{\nu_n \mu_1}(y_n, x_1).\end{aligned}\tag{2.65}$$

Of course, Eq. (2.65) reduces to the standard result in the case of the homogeneous electron gas [51–53]. Eq. (2.65) thus provides an alternative to Eq. (2.49) for all systems without a gap at the Fermi surface. In practice, a combination of the RPA with the second order functional (2.49) suggests itself as a rather universal form for  $E_{xc}$ .

### 3. Relativistic Optimized-Potential-Method

In Section 2 we have presented two systematic schemes, that allow the extraction of orbital- and eigenvalue-dependent representations of  $E_{xc}$ . As already emphasized, however, we are still dealing with current functionals, albeit implicit ones: In fact, the Hohenberg-Kohn theorem for noninteracting particles guarantees that the  $\phi_k$  and  $\epsilon_k$  are uniquely determined by  $j^\mu$  (up to gauge transformations), as long as they are solutions of single particle equations with a multiplicative potential. The functional dependences  $\phi_k([j]; \mathbf{r})$  and  $\epsilon_k[j]$  are established implicitly via the solution of the single particle equations. Consequently, we can follow the standard scheme for the derivation of the single particle equations (2.6) as in the case of explicitly  $j$ -dependent  $E_{xc}$ .

Both for the proper definition of the functional (2.45) and for selfconsistent calculations with orbital- and eigenvalue-dependent forms for  $E_{xc}$ , one then has to provide a method for the evaluation of the corresponding  $xc$ -potential  $\delta E_{xc} / \delta j^\mu$ . The basic approach to  $\delta E_{xc} / \delta j^\mu$  is provided by the OPM, which has first been introduced in the context of nonrelativistic DFT [21,20,5,27,54] and recently been extended to the relativistic domain [16,17,19,55]. The derivation of the crucial OPM integral equation determining the  $xc$ -potential can proceed along two different, but equivalent, lines [12,21]: In the original approach [21] the ground state energy  $E$  is explicitly minimized with respect to the total KS potential  $v_{KS}^\mu$ , which, due to the uniqueness of  $v_{KS}^\mu$ , indirectly yields the  $xc$ -component of  $v_{KS}^\mu$ . The second derivation [12] starts directly from Eq. (2.45), replacing the functional derivative with respect to  $j^\mu$  by derivatives

with respect to  $\phi_k^{(\dagger)}$  and  $\epsilon_k$  via the chain rule for functional differentiation. We here follow the latter scheme.

Bearing in mind the inherently recursive character of our first construction scheme for  $E_{xc}$ , Eqs. (2.44–2.49), one can again choose between two alternative approaches. On the one hand, it is possible to start with an expansion of  $E_{xc}$  in powers of  $e^2$ , as outlined in Section 2.3, and subsequently extract the  $xc$ -potential order by order. In this case it is important to note, that the lowest order contribution to  $E_{xc}$ , i.e. the exchange energy, only depends on the  $\phi_k^{(\dagger)}$  and  $\epsilon_k$ . This allows the calculation of  $v_x^\mu$  as a functional of the  $\phi_k^{(\dagger)}$  and  $\epsilon_k$  via the ROPM integral equation for the exchange functional. As a consequence, one can eliminate  $v_x^\mu$  from all higher orders terms in  $E_{xc}$  in favor of the  $\phi_k^{(\dagger)}$  and  $\epsilon_k$ . The second order contribution to  $E_{xc}$  then becomes a functional of the  $\phi_k^{(\dagger)}$  and  $\epsilon_k$  only, allowing to repeat the procedure. On the other hand, this recursive scheme for the coupled determination of  $v_{xc}$  and  $E_{xc}$  is not required from the very outset for establishing the ROPM integral equation. We thus first discuss the ROPM integral equation for the general nonlinear form (2.45), indicating a possible shortcut which resolves the coupling of  $v_{xc}^\mu$  and  $E_{xc}$ . Subsequently, the general result will be expanded in powers of  $e^2$ .

### 3.1. Complete nonlinear ROPM integral equations

Treating  $v_{xc}^\mu$  as an independent variable, the chain rule for functional differentiation gives

$$\begin{aligned} \frac{\delta E_{xc}[\phi_k^{(\dagger)}, \epsilon_k, v_{xc}^\mu]}{\delta j^\nu(\mathbf{r})} &= \int d^3 r' \frac{\delta v_{KS}^\rho(\mathbf{r}')}{\delta j^\nu(\mathbf{r})} \sum_k \left\{ \int d^3 r'' \left[ \frac{\delta \phi_k^\dagger(\mathbf{r}'')}{\delta v_{KS}^\rho(\mathbf{r}') \delta \phi_k^\dagger(\mathbf{r}'')} \frac{\delta E_{xc}}{\delta \phi_k^\dagger(\mathbf{r}'')} \right]_{expl.} + c.c. \right\} \\ &+ \frac{\delta \epsilon_k}{\delta v_{KS}^\rho(\mathbf{r}') \delta \epsilon_k} \frac{\delta E_{xc}}{\delta \epsilon_k} \Big|_{expl.} \Big\} + \int d^3 r' \frac{\delta v_{xc}^\rho(\mathbf{r}')}{\delta j^\nu(\mathbf{r})} \frac{\delta E_{xc}}{\delta v_{xc}^\rho(\mathbf{r}') \delta \phi_k^\dagger(\mathbf{r}'')} \Big|_{expl.}, \end{aligned} \quad (3.1)$$

where both the unique correspondence between  $j^\mu$  and  $v_{KS}^\mu$  and the unique correspondence between  $v_{KS}^\mu$  and the  $\phi_k^{(\dagger)}$ ,  $\epsilon_k$  have been used. In the following the derivatives of  $E_{xc}$  will always be understood with respect to the explicit dependence on  $\phi_k^{(\dagger)}$ ,  $\epsilon_k$  and  $v_{xc}^\mu$ , so that the index *expl.* is dropped from now on. The linear response of the  $\phi_k^{(\dagger)}$  and  $\epsilon_k$  to a variation of  $v_{KS}^\rho$ , which appears in (3.1), can be directly obtained from first order perturbation theory,

$$\frac{\delta \phi_k^\dagger(\mathbf{r})}{\delta v_{KS}^\rho(\mathbf{r}')} = -\phi_k^\dagger(\mathbf{r}') \alpha_\rho G_k(\mathbf{r}', \mathbf{r}) \quad (3.2)$$

$$G_k(\mathbf{r}, \mathbf{r}') = \sum_{l \neq k} \frac{\phi_l(\mathbf{r}) \phi_l^\dagger(\mathbf{r}')}{\epsilon_l - \epsilon_k} \quad (3.3)$$

$$\frac{\delta \epsilon_k}{\delta v_{KS}^\rho(\mathbf{r})} = \phi_k^\dagger(\mathbf{r}) \alpha_\rho \phi_k(\mathbf{r}). \quad (3.4)$$

Multiplying Eq. (3.1) with the static limit of the KS response function (2.64),

$$\begin{aligned}\chi_0^{\mu\nu}(\mathbf{r}, \mathbf{r}') &= \frac{\delta j^\mu(\mathbf{r})}{\delta v_{KS,\nu}(\mathbf{r}')} = \int_{-\infty}^{\infty} d\tau \chi_0^{\mu\nu}(\mathbf{r}, \mathbf{r}', \tau) \\ &= - \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \phi_k^\dagger(\mathbf{r}) \alpha^\mu G_k(\mathbf{r}, \mathbf{r}') \alpha^\nu \phi_k(\mathbf{r}') + c.c.,\end{aligned}\quad (3.5)$$

and integrating over  $\mathbf{r}$  leads to the ROPM integral equations for the  $xc$ -potential,

$$\int d^3 r' \chi_0^{\mu\nu}(\mathbf{r}, \mathbf{r}') v_{xc,\nu}(\mathbf{r}') = \Lambda_{xc}^\mu(\mathbf{r}), \quad (3.6)$$

where the inhomogeneity is given by

$$\begin{aligned}\Lambda_{xc}^\mu(\mathbf{r}) &= - \sum_k \int d^3 r' \left[ \phi_k^\dagger(\mathbf{r}) \alpha^\mu G_k(\mathbf{r}, \mathbf{r}') \frac{\delta E_{xc}}{\delta \phi_k^\dagger(\mathbf{r}')} + c.c. \right] + \sum_k \phi_k^\dagger(\mathbf{r}) \alpha^\mu \phi_k(\mathbf{r}) \frac{\partial E_{xc}}{\partial \epsilon_k} \\ &\quad + \int d^3 r' \int d^3 r'' \chi_0^{\mu\nu}(\mathbf{r}, \mathbf{r}') \frac{\delta v_{xc}^\nu(\mathbf{r}'')}{\delta j^\nu(\mathbf{r}')} \frac{\delta E_{xc}}{\delta v_{xc}^\nu(\mathbf{r}'')}. \end{aligned}\quad (3.7)$$

The ROPM integral equation (3.6) has to be solved selfconsistently together with the single particle equations (2.6), i.e. (3.6) replaces the explicit evaluation of  $\delta E_{xc}/\delta j^\mu$  of the conventional KS procedure.

The most critical functional derivative in (3.7) is the static  $xc$ -kernel

$$\frac{\delta v_{xc}^\mu(\mathbf{r})}{\delta j^\nu(\mathbf{r}')} = f_{xc}^{\mu\nu}(\mathbf{r}, \mathbf{r}'),$$

which makes (3.6) a highly nonlinear equation for  $v_{xc}^\mu$ .  $f_{xc}^{\mu\nu}$  has to be evaluated in accordance with the actual approximation used for  $E_{xc}$ . Apart from the systematic recursive procedure discussed in Section 3.2 an approximation strategy is conceivable: For the second order functional (2.49) one can explicitly evaluate the  $v_x^\mu$ -dependent component, using the known ROPM exchange potential. For atoms and molecules one finds that this energy component essentially cancels with certain other contributions to  $E_c^{(2)}$  (see Section 4). This fosters the hope that those terms which almost cancel each other can be neglected in  $\Lambda_{xc}^\mu$ , so that  $f_{xc}^{\mu\nu}$  is no longer required for the solution of the ROPM integral equation. Alternatively, one could apply some approximation for  $f_{xc}^{\mu\nu}$ , as e.g. the LDA. This would immediately allow to deal with nonperturbative classes of diagrammatic contributions to (2.45), as e.g. the combination of the RPA functional (2.65) with (2.49).

### 3.2. Second order ROPM equations

In this Section we discuss the ROPM integral equations for the recursive scheme introduced in Sec. 2.2, restricting the analysis to the order  $e^4$ . An extension to higher order can proceed along the same lines. Expanding the energy and the potential into a power series with respect to  $e^2$ ,

$$E_{xc} \rightarrow E_x + E_{c,2} + \dots \quad (3.8)$$

$$\mathbf{v}_{xc} \rightarrow \mathbf{v}_x + \mathbf{v}_{c,2} + \dots, \quad (3.9)$$

also the ROPM equations (3.6) can be expanded, leading to one integral equation for each order in  $e^2$ ,

$$\int d^3 r_2 \chi_0^{\mu\nu}(\mathbf{r}_1, \mathbf{r}_2) v_{x,\nu}(\mathbf{r}_2) = \Lambda_x^\mu(\mathbf{r}_1) \quad (3.10)$$

$$\int d^3 r_2 \chi_0^{\mu\nu}(\mathbf{r}_1, \mathbf{r}_2) v_{c,\nu}^{(2)}(\mathbf{r}_2) = \Lambda_c^{(2),\mu}(\mathbf{r}_1), \quad (3.11)$$

where the inhomogeneities are given by

$$\begin{aligned} \Lambda_x^\mu(\mathbf{r}_1) = & - \sum_k \int d^3 r_2 \left[ \phi_k^\dagger(\mathbf{r}_1) \alpha^\mu G_k(\mathbf{r}_1, \mathbf{r}_2) \frac{\delta E_x}{\delta \phi_k^\dagger(\mathbf{r}_2)} + c.c. \right] \\ & + \sum_k \phi_k^\dagger(\mathbf{r}_1) \alpha^\mu \phi_k(\mathbf{r}_1) \frac{\partial E_x}{\partial \epsilon_k} \end{aligned} \quad (3.12)$$

$$\begin{aligned} \Lambda_c^{(2),\mu}(\mathbf{r}_1) = & - \sum_k \int d^3 r_2 \left[ \phi_k^\dagger(\mathbf{r}_1) \alpha^\mu G_k(\mathbf{r}_1, \mathbf{r}_2) \frac{\delta E_c^{(2)}}{\delta \phi_k^\dagger(\mathbf{r}_2)} + c.c. \right] \\ & + \sum_k \phi_k^\dagger(\mathbf{r}_1) \alpha^\mu \phi_k(\mathbf{r}_1) \frac{\partial E_c^{(2)}}{\partial \epsilon_k} + \int d^3 r_2 \frac{\delta v_x^\nu(\mathbf{r}_2)}{\delta v_{KS,\mu}(\mathbf{r}_1)} \frac{\delta E_c^{(2)}}{\delta v_x^\nu(\mathbf{r}_2)} \end{aligned} \quad (3.13)$$

(the unique correspondence between  $j^\mu$  and  $v_{KS}^\mu$  has been used to simplify the last term in Eq. (3.13)).

The evaluation of the functional derivatives of  $E_x$  and  $E_c^{(2)}$  can be performed directly using Eqs. (2.47, 2.49). The only nontrivial term appearing in the order  $e^4$  is  $\delta v_x^\nu / \delta v_{KS,\mu}$ . For its calculation we rely on the first order ROPM equation (3.10): Taking its functional derivative with respect to  $v_{KS}^\mu$ , one finds after reordering

$$\frac{\delta v_x^\nu(\mathbf{r}_2)}{\delta v_{KS}^\mu(\mathbf{r}_1)} = \int d^3 r_3 \chi_0^{-1,\nu\lambda}(\mathbf{r}_2, \mathbf{r}_3) \left\{ \frac{\delta \Lambda_{x,\lambda}(\mathbf{r}_3)}{\delta v_{KS}^\mu(\mathbf{r}_1)} - \int d^3 r_4 \frac{\delta \chi_{0,\lambda\rho}(\mathbf{r}_3, \mathbf{r}_4)}{\delta v_{KS}^\mu(\mathbf{r}_1)} v_x^\rho(\mathbf{r}_4) \right\}, \quad (3.14)$$

with  $\chi_0^{-1,\nu\lambda}$  denoting the inverse response function,

$$\int d^3 r' \chi_0^{-1,\mu\nu}(\mathbf{r}, \mathbf{r}') \chi_{0,\nu\rho}(\mathbf{r}', \mathbf{r}'') = \delta^{(3)}(\mathbf{r} - \mathbf{r}'') \delta_\nu^\mu.$$

The standard ROPM replacement of functional derivatives (again using the various unique equivalences) directly yields an expression for the first contribution on the right hand side of (3.14) in terms of the orbitals and eigenvalues,

$$\begin{aligned} \frac{\delta\Lambda_x^\lambda(\mathbf{r}_2)}{\delta\mathbf{v}_{KS}^\mu(\mathbf{r}_1)} &= - \sum_k \int d^3 r_3 \left[ \phi_k^\dagger(\mathbf{r}_1) \alpha_\mu G_k(\mathbf{r}_1, \mathbf{r}_3) \frac{\delta\Lambda_x^\lambda(\mathbf{r}_2)}{\delta\phi_k^\dagger(\mathbf{r}_3)} + c.c. \right] \\ &+ \sum_k \phi_k^\dagger(\mathbf{r}_1) \alpha_\mu \phi_k(\mathbf{r}_1) \frac{\partial\Lambda_x^\lambda(\mathbf{r}_2)}{\partial\epsilon_k}. \end{aligned} \quad (3.15)$$

The second contribution in (3.14) contains the quadratic response function,

$$\begin{aligned} \frac{\delta\chi_{0,\mu_1\mu_2}(\mathbf{r}_1, \mathbf{r}_2)}{\delta\mathbf{v}_{KS}^{\mu_3}(\mathbf{r}_3)} &= \frac{\delta^2 j_{\mu_1}(\mathbf{r}_1)}{\delta\mathbf{v}_{KS}^{\mu_3}(\mathbf{r}_3) \delta\mathbf{v}_{KS}^{\mu_2}(\mathbf{r}_2)} \\ &= \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} H_{k,\mu_1\mu_2\mu_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ &+ \text{all permutations of } \mathbf{r}_1\mu_1 \leftrightarrow \mathbf{r}_2\mu_2 \leftrightarrow \mathbf{r}_3\mu_3, \end{aligned} \quad (3.16)$$

with

$$\begin{aligned} H_{k,\mu_1\mu_2\mu_3}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= \phi_k^\dagger(\mathbf{r}_1) \alpha_{\mu_1} G_k(\mathbf{r}_1, \mathbf{r}_2) \alpha_{\mu_2} G_k(\mathbf{r}_2, \mathbf{r}_3) \alpha_{\mu_3} \phi_k(\mathbf{r}_3) \\ &- \phi_k^\dagger(\mathbf{r}_1) \alpha_{\mu_1} \phi_k(\mathbf{r}_1) \phi_k^\dagger(\mathbf{r}_2) \alpha_{\mu_2} \int d^3 r_4 G_k(\mathbf{r}_2, \mathbf{r}_4) G_k(\mathbf{r}_4, \mathbf{r}_3) \alpha_{\mu_3} \phi_k(\mathbf{r}_3). \end{aligned} \quad (3.17)$$

Eqs. (3.10–3.17) together with (2.47, 2.49, 3.3, 3.5) provide all the necessary ingredients for the determination of  $v_x$  and  $v_c^{(2)}$ . However, it is immediately clear from these relations that a higher order perturbative treatment of  $E_{xc}$ , requiring still higher order response functions, becomes prohibitive on the selfconsistent level.

Finally, we note that Eqs. (3.5–3.7) can also be used to extract the behavior of the  $xc$ -potential in the asymptotic regime of finite systems. Restricting the analysis to spherically averaged systems, a somewhat tedious analysis (the interested reader is referred to [19]) leads to the relativistic form of the Krieger-Li-Iafrate identity for the highest occupied orbital  $\phi_h$  [56],

$$\int d^3 r \phi_h^\dagger(\mathbf{r}) \left\{ \phi_h(\mathbf{r}) v_x^0(\mathbf{r}) - \frac{\delta E_x}{\delta\phi_h^\dagger(\mathbf{r})} \right\} + c.c. = 0, \quad (3.18)$$

and the asymptotic behavior of  $v_x^0$ ,

$$v_x^0(r) \xrightarrow{r \rightarrow \infty} -\frac{e^2}{r}, \quad (3.19)$$

which one would have expected from the analogous nonrelativistic relation [21].

#### 4. First Results for the Coulomb Limit

In order to facilitate a direct comparison with other relativistic many-body methods as the RHF approach and the Møller-Plesset perturbation expansion [30] we now reduce

the main results of Section 2 to the limit of a pure Coulomb interaction between the electrons (longitudinal limit). The resulting expressions also allow for the straightforward extraction of the nonrelativistic limit, simply by replacing the four spinors  $\phi_k$  by the corresponding Pauli spinors. The Coulomb limit is obtained by substituting the photon propagator  $D_{\mu\nu}^0$  by the instantaneous Coulomb interaction,

$$D_{\mu\nu}^0(x-y) \rightarrow \frac{e^2 g_{\mu 0} g_{\nu 0}}{|\mathbf{x}-\mathbf{y}|} \delta(x^0-y^0), \quad (4.1)$$

and appropriately reordering the field operators in the interaction Hamiltonian,

$$\hat{j}_0^0(x)\hat{j}_0^0(y)|_{x^0=y^0=ct} \rightarrow \hat{\psi}_0^\dagger(\mathbf{x}t)\hat{\psi}_0^\dagger(\mathbf{y}t)\hat{\psi}_0(\mathbf{y}t)\hat{\psi}_0(\mathbf{x}t). \quad (4.2)$$

In this way one ends up with the familiar forms of the Hartree and exchange energies,

$$E_H^C = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad (4.3)$$

$$E_x^C = -\frac{e^2}{2} \int d^3r \int d^3r' \sum_{-mc^2 < \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\phi_k^\dagger(\mathbf{r})\phi_l(\mathbf{r})\phi_l^\dagger(\mathbf{r}')\phi_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \quad (4.4)$$

while the complete  $E_c$  is given by (2.45) evaluated with the Coulomb form of  $\hat{W}$ ,

$$\begin{aligned} \hat{W}^C(t) &= \frac{e^2}{2} \int d^3x \int d^3y \frac{\hat{\psi}_0^\dagger(\mathbf{x}t)\hat{\psi}_0^\dagger(\mathbf{y}t)\hat{\psi}_0(\mathbf{y}t)\hat{\psi}_0(\mathbf{x}t)}{|\mathbf{x}-\mathbf{y}|} \\ &\quad - \int d^3x \{v_{H,0}(\mathbf{x})g_{0\mu} + v_{xc,\mu}(\mathbf{x})\} \hat{\psi}_0^\dagger(\mathbf{x}t)\alpha^\mu \hat{\psi}_0(\mathbf{x}t). \end{aligned} \quad (4.5)$$

In particular, the Coulomb limit of the lowest order correlation contribution  $E_c^{(2)}$  reads

$$E_c^{(2),C} = E_{MP2} + E_{\Delta HF} \quad (4.6)$$

$$\begin{aligned} E_{MP2} &= \frac{e^4}{2} \sum_{-mc^2 < \epsilon_i, \epsilon_j \leq \epsilon_F < \epsilon_k, \epsilon_l} \frac{1}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l} \int d^3r_1 \int d^3r_2 \frac{\phi_i^\dagger(\mathbf{r}_1)\phi_k(\mathbf{r}_1)\phi_j^\dagger(\mathbf{r}_2)\phi_l(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \\ &\quad \times \int d^3r_3 \int d^3r_4 \left\{ \frac{\phi_k^\dagger(\mathbf{r}_3)\phi_i(\mathbf{r}_3)\phi_l^\dagger(\mathbf{r}_4)\phi_j(\mathbf{r}_4)}{|\mathbf{r}_3-\mathbf{r}_4|} - \frac{\phi_k^\dagger(\mathbf{r}_3)\phi_j(\mathbf{r}_3)\phi_l^\dagger(\mathbf{r}_4)\phi_i(\mathbf{r}_4)}{|\mathbf{r}_3-\mathbf{r}_4|} \right\} \end{aligned} \quad (4.7)$$

$$\begin{aligned} E_{\Delta HF} &= \sum_{-mc^2 < \epsilon_k \leq \epsilon_F < \epsilon_l} \frac{1}{\epsilon_k - \epsilon_l} \left| \int d^3r_1 \phi_k^\dagger(\mathbf{r}_1)\alpha^\mu \phi_l(\mathbf{r}_1)v_{x,\mu}^C(\mathbf{r}_1) \right. \\ &\quad \left. + e^2 \sum_{-mc^2 < \epsilon_j \leq \epsilon_F} \int d^3r_1 \int d^3r_2 \frac{\phi_k^\dagger(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\phi_j^\dagger(\mathbf{r}_2)\phi_l(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \right|^2. \end{aligned} \quad (4.8)$$

Its first term,  $E_{MP2}$ , has exactly the same functional form as the conventional second order Møller-Plesset correlation contribution (MP2). However, in Eqs. (4.7, 4.8) the  $\phi_k^{(\dagger)}$  represent KS orbitals, which experience the multiplicative KS potential (2.7), rather

than the nonlocal HF potential. The difference between both potentials is most obvious for neutral atoms, for which they produce a completely different spectrum of virtual excitations: While the HF potential is short-ranged and therefore generates no bound states beyond the  $N$  occupied orbitals [57], the asymptotic  $-e^2/r$  tail of  $v_x^0$ , Eq. (3.19), leads to a complete Rydberg series in the case of  $v_{KS}$ . The second term,  $E_{\Delta HF}$ , reflects the conceptual difference between the  $x$ -only ROPM and the RHF approach, i.e. it represents the lowest order perturbative contribution to the difference  $\Delta E$  between the RHF and the  $x$ -only ROPM ground state energies,

$$\Delta E = E^{RHF} - E^{x\text{-only ROPM}}. \quad (4.9)$$

We just remark that  $E_c^{(2)C}$  also includes the leading contribution to the van-der-Waals interaction between two atoms [19].

To illustrate the relation between the  $x$ -only ROPM and the RHF scheme we list the resulting ground state energies of closed subshell atoms in Table 1. All results in Table 1 have been calculated fully numerically on a discretized radial grid of 400–800 mesh points, using standard finite differences techniques for the solution of the radial Dirac equation and for integration. As is immediately obvious from Table 1 the ROPM values are extremely close to the RHF energies, their difference reflecting the slightly reduced variational freedom of the ROPM: While the ground state energy expressions of the  $x$ -

Table 1 *X-only Coulomb ground state energies: Selfconsistent ROPM [16], RHF [60], RLDA and PW91-GGA [8] results for neutral atoms with closed subshells. Also given is  $E_{\Delta HF}$ , Eq. (4.8) (all energies in hartree).*

Atom	$E^C$	$E^C - E^{C,ROPM}$			$E_{\Delta HF}$
	ROPM	RLDA	PW91	RHF	
He	-2862	138	6	0	0
Be	-14575	350	18	-1	-1
Ne	-128690	1062	-26	-2	-2
Mg	-199932	1376	-5	-3	-3
Ar	-528678	2341	21	-5	-6
Ca	-679704	2656	-4	-6	-7
Zn	-1794598	4140	-388	-14	-16
Kr	-2788848	5565	-265	-13	-13
Sr	-3178067	5996	-305	-13	-13
Pd	-5044384	7707	-666	-16	-17
Cd	-5593299	8213	-734	-20	-22
Xe	-7446876	9800	-1003	-19	-20
Ba	-8135625	10289	-1188	-19	-20
Yb	-14067621	13272	-3789	-48	-57
Hg	-19648826	17204	-5132	-39	-41
Rn	-23601969	19677	-6530	-35	-38
Ra	-25028027	20460	-7186	-34	-37
No	-36740625	25787	-14645	-57	-67

only ROPM and RHF are identical, the restriction to a multiplicative exchange potential in the case of the ROPM leads to marginally higher energies. This difference is essentially given by  $E_{\Delta HF}$ , Eq. (4.8), as can also be seen from Table 1.

In order to demonstrate the qualitative progress accompanying the use of the orbital-dependent  $E_x$  we also list the ground state energies obtained with the relativistic  $x$ -only LDA [32,33] and the exchange component of the Perdew-Wang (PW91) GGA [8]. While the relativistic LDA (RLDA) misrepresents  $E^C$  throughout the periodic table, the GGA is clearly more accurate for light atoms. The fact that the deviation of the GGA energies from the ROPM values strongly increases with  $Z$  indicates the need for the inclusion of relativistic corrections in GGAs. While this problem can be resolved by introducing appropriate relativistic correction factors [58], the performance of the resulting relativistic GGAs is still not completely satisfying. This is most obvious from the fact that the GGA exchange potential for finite systems decays much faster than  $-e^2/r$  for large  $r$ , leading e.g. to a rather poor description of negative ions.

In Table 2 we show the Coulomb correlation energies of the neon isoelectronic series obtained with the functional (4.6) by insertion of selfconsistent  $x$ -only ROPM orbitals, in comparison with MP2 results [30] (the neon isoelectronic series appears to be the only systematic set of data beyond the helium series for which accurate relativistic MP2 data are available in the literature, so that it is ideally suited for this comparison). All necessary  $r$ -integrations have been performed on a radial grid of 1600 mesh points, using the numerical spinors resulting from  $x$ -only ROPM calculations, both for the bound part of the spectrum and the positive continuum. The contribution of higher Rydberg states have been treated by an analytical formula derived by Kelly [59]. This resummation rests on the observation that the ratio of two expectation values, which differ only in the principal quantum number  $n$  of one state involved approaches a simple form in the limit of large  $n_A, n'_A$ ,

Table 2 Correlation energies of the neon isoelectronic series: Comparison of  $E_{c,2}^C$ , Eq. (4.6), with the corresponding second order Møller-Plesset (MP2) [30], RLDA [16] and PW91-GGA [8] results. In addition,  $E_{\Delta HF}$ , Eq. (4.8), is compared with the difference  $\Delta E$ , Eq. (4.9), between RHF [60] and  $x$ -only ROPM [16] total energies (all energies in mhartree).

Atom	$-E_c^{MP2}$	$-E_c^{(2),C}$	$-E_c^{LDA}$	$-E_c^{PW91}$	$-E_{\Delta HF}$	$-\Delta E$
Ne	383.2	476.5	747	382	1.7	1.7
Ca <sup>10+</sup>	395.4	430.4	1010	474	2.1	2.0
Zn <sup>20+</sup>	406.4	430.8	1147	509	2.2	2.2
Zr <sup>30+</sup>	414.1	434.1	1243	529	2.4	2.4
Sn <sup>40+</sup>	421.6	439.3	1317	544	2.8	2.7
Nd <sup>50+</sup>	430.2	446.8	1380	554	3.4	3.2
Yb <sup>60+</sup>	441.1	457.6	1434	562	4.4	4.0
Hg <sup>70+</sup>	455.5	472.8	1484	568	6.0	5.2
Th <sup>80+</sup>	475.4	494.9	1530	571	8.6	7.2
Fm <sup>90+</sup>	504.4	528.2	1575	573	13.0	11.0

$$\frac{\langle n_A, l_A, j_A; B | \hat{O} | C; D \rangle}{\langle n'_A, l_A, j_A; B | \hat{O} | C; D \rangle} \sim \left( \frac{n'_A}{n_A} \right)^{3/2} \quad (4.10)$$

(the orbitals  $B$ ,  $C$ ,  $D$  are unchanged, as are the angular momenta  $l_A$  and  $j_A$ ). For discrete excited states with  $l = 0, 1$  Eq. (4.10) was used to resum the contributions of shells with principal quantum number  $n \geq 15$ . In contrast, for orbitals with  $l = 2, 3, 4$  Eq. (4.10) was already utilized for  $n \geq 6$ . The integration over the continuum states has also been done via a Newton-Cotes algorithm, checking carefully that the number of energy mesh points ( $\sim 50$ – $100$ ) is sufficient to achieve the desired accuracy of  $0.1$  *hartree*. All angular momenta up to  $l = 10$  have been included for the continuum states, and the corresponding energy cutoff has been chosen to be the absolute value of 400 times the innermost eigenvalue of the ion under investigation.

Focussing on the total correlation energies reported in the first two columns of Table 2, one notices a marked difference of 20% between the conventional MP2 and the corresponding DFT correlation energy (4.6) of neon. This deviation, however, diminishes rapidly to approximately 5% for neonlike zinc. For still higher  $Z$  the relative difference remains almost constant. The particular discrepancy for neon can in large part be attributed to the excitations into the Rydberg states, which give a contribution of  $-43.7$  *hartrees*. On the other hand, as  $Z$  increases along the isoelectronic series, the asymptotic behavior of the HF and KS potentials becomes more and more similar, and thus also the excitation spectra approach each other. It remains to be investigated how energy differences as ionization potentials or electron affinities obtained with the two schemes compare with each other.

Table 2 also shows the well-known incorrect  $Z$ -scaling of the LDA correlation energies for isoelectronic series: The error of the LDA increases from almost a factor of 2 to more than a factor of 3 from neon to fermium. On the other hand, the nonrelativistic PW91-GGA [8] agrees closely with the MP2 result for neon. However, while the GGA improves substantially over the LDA also for higher  $Z$ , the data nevertheless indicate that its scaling with  $Z$  is not completely satisfactory. The fact that the deviation of the GGA is as large for  $\text{Ca}^{10+}$  as it is for  $\text{Fm}^{10+}$  demonstrates that this error cannot be explained by the missing relativistic corrections in the functional form of the GGA. In any case, apart from neon,  $E_c^{(2),C}$  gives clearly more accurate correlation energies than the GGA. In particular,  $E_c^{(2),C}$  shows the correct  $Z$ -scaling (this is also true in the nonrelativistic limit).

Finally, in Table 2 one again recognizes that  $E_{\Delta HF}$  gives a good account of the difference  $\Delta E$  between the  $x$ -only ROPM and the RHF ground state energies. Although no corresponding estimate of the quantitative impact of  $E_{\Delta HF}$  on the selfconsistent  $v_c^{(2)}$ , Eq. (3.13), is presently available, the small size of  $E_{\Delta HF}$ , as compared to  $E_{MP2}$ , suggests that neglect of  $E_{\Delta HF}$  could be a reasonable approximation to (4.6). This would eliminate the  $v_x$ -dependence of  $E_c^{(2),C}$ , thus considerably simplifying the ROPM procedure for this functional.

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