

Relativistic Density Functional Theory

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1 Introduction

A few numbers will illustrate that it is necessary to develop a relativistic version of density functional theory (DFT) [1, 2, 3, 4, 5, 6]. The relative relativistic correction

$$\frac{A_{rel} - A_{nrel}}{A_{nrel}}$$

is about 30% for the ionisation potential of the Gold atom, -13% for the bond length of the AuH molecule and about 50% for the dissociation energy of this system [7]. The error can even be larger for sensitive quantities like the electron affinity. For this quantity one finds

$$A_{nrel} = 0.10eV \quad A_{rel} = 0.67eV$$

on the level of the Hartree Fock (HF) approximation [8], and

$$A_{nrel} = 1.02eV \quad A_{rel} = 2.28eV$$

on the level of the configuration interaction approach [7, 9]. Obviously, relativistic and correlation effects modify results on a comparable level.

While it is still possible to deal with relativistic effects in smaller systems in terms of traditional methods, the treatment of larger systems with heavier constituents will require a relativistic extension of DFT (RDFT). One of the questions that has to be answered in this context is: How much of the relativistic correction is due to kinetic effects (replace the nonrelativistic kinetic energy by its relativistic counterpart) and how much is due to exchange-correlation effects? The answer to this and other questions is the goal of our endeavours.

The proper frame for the discussion of RDFT is a suitable field theoretical formulation [10, 11, 12] of the problem at hand. For the case of Coulomb systems such a theory is quantum electrodynamics (QED). One might ask: Why not base the discussion on the many-body Dirac equation, as eg. in standard Dirac-Fock calculations?

Here is a more extensive answer. As one knows, Dirac theory leads to a positive definite one particle density

$$n(\underline{x}) = \bar{\psi}(x)\gamma^0\psi(x) = \psi^\dagger(x)\psi(x) .$$

On the other hand, the energy spectrum contains a negative energy continuum. In order to prevent disaster, one has to invoke the concept of a filled Dirac sea. Holes in this sea can be associated with antiparticles.

One possibility to handle this situation in an economic fashion is the transition to a field theoretical formulation, which is, for present purposes, indicated for the case of the free particle problem. The free Dirac equation (with $\hbar = c = 1$, as usual) is

$$(-i\rlap{\not{\partial}} + m)\psi(x) = 0 \quad , \quad \rlap{\not{\partial}} = \gamma^\mu \partial_\mu = \gamma^\mu \frac{\partial}{\partial x^\mu} . \quad (1)$$

A general solution of this equation (a spinor wave packet) is

$$\psi(x) = \int d^3k \sum_{l=1}^2 \left[b_l(k) u^{(l)}(k) e^{-ik \cdot x} + c_l(k) v^{(l)}(k) e^{ik \cdot x} \right] , \quad k_0 = \sqrt{\mathbf{k}^2 + m^2} .$$

The notation is

- positive, negative energy spinors $u^{(l)}, v^{(l)}$
- energy-momentum four vector $k = (k_0, \mathbf{k})$
- Minkowski space scalar product $k \cdot x = k_0 t - \mathbf{k} \cdot \mathbf{x}$.

In the process of field quantisation the spinor wave functions are replaced by field operators,

$$\psi(x), \psi^+(x) \quad \longrightarrow \quad \hat{\psi}(x), \hat{\psi}^+(x) ,$$

by demanding that canonical, equal time anticommutation relations hold,

$$\{ \hat{\psi}_\alpha(\mathbf{x}, t), \hat{\psi}_\beta^+(\mathbf{y}, t) \} = \delta_{\alpha\beta} \delta^{(3)}(\mathbf{x} - \mathbf{y}) \quad (\alpha, \beta = 1, \dots, 4) . \quad (2)$$

This requires that the Fourier coefficients b_l, c_l be replaced by operators,

$$\begin{aligned} b_l(k) &\rightarrow \hat{b}_l(k) & b_l^*(k) &\rightarrow \hat{b}_l^+(k) \\ c_l(k) &\rightarrow \hat{c}_l(k) & c_l^*(k) &\rightarrow \hat{c}_l^+(k) . \end{aligned}$$

In order to incorporate the concept of the Dirac sea directly, one reinterprets the operators associated with the negative energy solutions as

$$\hat{c}_l(k) \rightarrow \hat{d}_l^+(k) \quad \hat{c}_l^+(k) \rightarrow \hat{d}_l(k) ,$$

the interpretation being: The destruction of a particle with negative energy corresponds to the creation of an antiparticle with positive energy (and vice versa). This language refers to a vacuum state that is free of particles rather than the filled sea,

$$\hat{b}_l(k) |vac\rangle = 0 \quad , \quad \hat{d}_l(k) |vac\rangle = 0 .$$

The corresponding relativistic field operator

$$\hat{\psi}(x) = \int d^3k \sum_{l=1}^2 \left[\hat{b}_l(k) u^{(l)}(k) e^{-ik \cdot x} + \hat{d}_l^+(k) v^{(l)}(k) e^{ik \cdot x} \right] \quad (3)$$

then describes the destruction of a particle or the creation of an antiparticle. $\hat{\psi}^+(x)$ describes the creation of a particle and the destruction of an antiparticle. Other operators can then be constructed like

(i) the charge operator

$$\hat{Q} = -e \int d^3k \sum_{l=1}^2 [\hat{b}_l^+(k) \hat{b}_l(k) - \hat{d}_l^+(k) \hat{d}_l(k)] \quad (4)$$

$$= -e(\hat{N}_{part} - \hat{N}_{antipart}) \quad , \quad (5)$$

where infinite but trivial vacuum expectation values have been subtracted. One then notes that $\hat{\psi}(x)$ raises the charge by one unit, while $\hat{\psi}^+(x)$ decreases the charge correspondingly.

(ii) the free Hamiltonian

$$\hat{H} = \int d^3x \hat{\bar{\psi}}(x) (-i\boldsymbol{\gamma} \cdot \boldsymbol{\nabla} + m) \hat{\psi}(x) \quad (6)$$

$$\begin{aligned} &= \int d^3k \sum_{l=1}^2 [\hat{b}_l^+(k) \hat{b}_l(k) - \hat{d}_l(k) \hat{d}_l^+(k)] k_0 \\ &= \int d^3k \sum_{l=1}^2 [\hat{b}_l^+(k) \hat{b}_l(k) + \hat{d}_l^+(k) \hat{d}_l(k)] k_0 + \infty \quad , \end{aligned} \quad (7)$$

so that one can redefine the trivially renormalised Hamiltonian

$$\hat{H}_R \equiv \hat{H} - \langle vac | \hat{H} | vac \rangle = \int d^3k k_0 \{ \hat{N}_{part}(k) + \hat{N}_{antipart}(k) \} \quad (8)$$

Contrasting once more energy and charge in Dirac and field theory we note for a free particle (charge $-e$)/antiparticle:

	charge	energy
Dirac theory	negative definite	positive/negative
field theory	negative/positive	positive definite

Obviously, the second line corresponds to the experimental solution.

In addition, the field theoretical formulation of the interacting problem (the coupling to the electromagnetic field can be introduced by invoking local $U(1)$ gauge invariance) involves for instance the features:

(i) The interaction between the fermions is described by the photon propagator rather than the Coulomb interaction. In lowest order this propagator describes the exchange of a free photon,

$$D_{\mu\nu}^{(0)}(x, y) \longrightarrow \text{~~~~~} \quad .$$

It contains retardation and magnetic effects. One may even consider more exact forms like

$$D_{\mu\nu}(x, y) = \text{~~~~~} + \text{~~~~~} \bigcirc \text{~~~~~} + \dots ,$$

involving lowest order vacuum polarisation effects.

- (ii) The full machinery of many-body physics [13, 14] can be activated directly, with fermion propagators, Dyson equations etc.

If one accepts these statements as an answer to the question posed, then one can start to look at a selection of the background material that is necessary for the discussion of RDFT. This is done in section 2, which is entitled

2 Assorted Remarks on Vacuum QED, the Relativistic Homogeneous Electron Gas and QED with External Potentials

A system of Dirac particles (charge $-e$) and antiparticles, which interact by the exchange of photons is characterised by the QED Lagrangian density

$$\mathcal{L}_{QED}(x) = \mathcal{L}_e(x) + \mathcal{L}_\gamma(x) + \mathcal{L}_{int}(x) . \quad (9)$$

The three terms represent the free Dirac Lagrangian of the fermions

$$\mathcal{L}_e(x) = \frac{i}{2} [\hat{\bar{\psi}}(x) \gamma^\mu \partial_\mu \hat{\psi}(x) - (\partial_\mu \hat{\bar{\psi}}(x)) \gamma^\mu \hat{\psi}(x)] - m \hat{\bar{\psi}}(x) \hat{\psi}(x) , \quad (10)$$

the free photon Lagrangian

$$\mathcal{L}_\gamma(x) = -\frac{1}{16\pi} \hat{F}_{\mu\nu}(x) \hat{F}^{\mu\nu}(x) - \frac{\lambda}{8\pi} (\partial_\nu \hat{A}^\nu(x))^2 \quad (11)$$

and the interaction term

$$\mathcal{L}_{int}(x) = -e \hat{j}^\nu(x) \hat{A}_\nu(x) . \quad (12)$$

The following explanatory remarks are necessary.

- (i) $\hat{\psi}(x)$ and $\hat{A}_\mu(x)$ are the fermion and photon field operators, the actual electromagnetic field is characterised by the field tensor

$$\hat{F}_{\mu\nu}(x) = \partial_\mu \hat{A}_\nu(x) - \partial_\nu \hat{A}_\mu(x) . \quad (13)$$

$\hat{j}^\nu(x)$ is the fermion four current. It is most conveniently specified in the commutator form

$$\hat{j}^\nu(x) = \frac{1}{2} [\hat{\bar{\psi}}(x), \gamma^\nu \hat{\psi}(x)] , \quad (14)$$

which explicitly expresses charge conjugation invariance.

- (ii) The quantisation of the free photon problem is more complicated due to the transversality of the photon field. The form of the Lagrangian specified refers to a covariant gauge (and thus involves the so-called gauge fixing term). Standard gauges are the Feynman gauge ($\lambda = 1$) and the Landau gauge ($\lambda = \infty$). The photon sector of the Fock space is supposed to be specified in terms of the Gupta-Bleuler indefinite metric quantisation. We will, however, not display any details concerning this point.

Essentially, all results available for (vacuum) QED systems are based on perturbation theory. The basic quantities used in this context are the fermion and the photon propagators (where T denotes time-ordering)

$$S_{F,vac}(x, y)_{\alpha\beta} = -i \langle vac | T \hat{\psi}_\alpha(x) \hat{\bar{\psi}}_\beta(y) | vac \rangle \quad (15)$$

$$= \int \frac{d^4 p}{(2\pi)^4} S_{F,vac}(p)_{\alpha\beta} e^{-ip \cdot (x-y)} \quad (16)$$

$$D_{\mu\nu,vac}(x, y) = -ie^2 \langle vac | T \hat{A}_\mu(x) \hat{A}_\nu(y) | vac \rangle \quad (17)$$

$$= \int \frac{d^4 q}{(2\pi)^4} D_{\mu\nu,vac}(q) e^{-iq \cdot (x-y)} \quad (18)$$

The fact that both quantities depend only on the difference of the Minkowski coordinates is an expression of the translational invariance of the theory.

In lowest order, these propagators can be calculated directly. For the fermion propagator (describing the time development of a free fermion forward and of a free anti-fermion backward in time) one finds

$$S_{F,vac}^{(0)}(p)_{\alpha\beta} = \left(\frac{\not{p} + m}{p^2 - m^2 + i\epsilon} \right)_{\alpha\beta} \quad (19)$$

In diagrammar this quantity will be denoted by

$$S_{F,vac}^{(0)}(p)_{\alpha\beta} = \alpha \xrightarrow{p} \beta \quad (20)$$

The photon propagator depends on the choice of gauge. In Landau gauge one finds

$$D_{\mu\nu}^{(0)}(q) = -\frac{4\pi e^2}{q^2 + i\epsilon} \left\{ g_{\mu\nu} - \frac{q_\mu q_\nu}{q^2} \right\} \quad (21)$$

the second term in the bracket is not present in Feynman gauge. In diagrammar we represent this quantity by

$$iD_{\mu\nu}^{(0)}(q) = \mu \overset{q}{\sim} \nu \quad (22)$$

We shall later use the decomposition of this propagator into a nonretarded Coulomb (longitudinal) and a transverse contribution,

$$D_{\mu\nu}^{(0)}(q) = D_{\mu\nu}^{(0)L}(q) + D_{\mu\nu}^{(0)T}(q) \quad (23)$$

If one evaluates the integrals over the loop momenta, one finds that neither of the three quantities $\Sigma^{(1)}$, $\Pi^{(0)}$ and $\Gamma^{(1)}$ is well defined. One encounters UV-divergencies (divergencies due to large values of the loop momenta). One way to deal with these divergencies and to endow the three quantities with a meaning is the counterterm technique based on dimensional regularisation [15]. In this method one first evaluates the integrals indicated in $(1, d - 1)$ -dimensional Minkowski space (rather than in the $(1, 3)$ -dimensional space). These results can then be analytically continued to noninteger d , so that the physically interesting limit $d \rightarrow 4$ can be taken. The results (involving an expansion about this limit) are

$$\Sigma_{vac}^{(1)}(p) = \frac{\epsilon^2}{16\pi^2} \Gamma(s) (-\not{p} + 4m) + \Sigma_{vac,finite}^{(1)}(p) \quad (31)$$

$$\Pi_{\mu\nu,vac}^{(0)}(q) = (q^2 g_{\mu\nu} - q_\mu q_\nu) \left\{ \frac{\Gamma(s)}{12\pi^2} + \omega_{vac,finite}^{(0)}(q^2) \right\} \quad (32)$$

$$\Gamma_{\mu,vac}^{(1)}(p_1, p_2) = \frac{\epsilon^2}{16\pi^2} \Gamma(s) \gamma_\mu + \Gamma_{\mu,vac,finite}^{(1)}(p_1, p_2) \quad (33)$$

The divergent part of the loop integrals is isolated in each case in the Γ -function

$$\Gamma(s) \equiv \Gamma\left(\frac{1}{2}(4-d)\right) \xrightarrow{s \rightarrow 0} \frac{1}{s} + \dots \quad (34)$$

For the finite remainders, the limit $d \rightarrow 4$ can be taken directly. The rather lengthy expressions that result are not of interest for the moment.

Two additional features might be of interest though: The tensorial structure of the vacuum polarisation is a consequence of the general gauge invariance,

$$q^\mu \Pi_{\mu\nu}(q) = 0 \quad (35)$$

Another manifestation of gauge invariance is the Ward-Takahashi identity,

$$(p_\mu - p'_\mu) \Gamma_{vac}^\mu(p, p') = \Sigma_{vac}(p') - \Sigma_{vac}(p) \quad (36)$$

which is satisfied by the divergent (as well as the finite) contributions to Σ and Γ .

The next step, the actual renormalisation, amounts to a redefinition of the physical constants and operators in the initial Lagrangian, leaving the physical implications of this Lagrangian unmodified. The renormalisation procedure can readily be demonstrated (on the one loop level) for the case of mass renormalisation. Using the Dyson equation

$$S_{F,vac}(p)^{-1} = S_{F,vac}^{(0)}(p)^{-1} - \Sigma_{vac}(p) = \not{p} - m - \Sigma_{vac}(p) \quad (37)$$

one finds to first order

$$S_{F,vac}^{(1)}(p)^{-1} = \not{p} \left(1 + \frac{\epsilon^2}{16\pi^2} \Gamma(s) \right) - m \left(1 + \frac{\epsilon^2}{4\pi^2} \Gamma(s) \right) - \Sigma_{vac,finite}^{(1)}(p) \quad (38)$$

In order to compensate the terms that diverge in the limit $d \rightarrow 4$, one adds to the "unrenormalised Lagrangian" a "counterterm Lagrangian" of the same form.

The unrenormalised Lagrangian has the form (9) originally given with physical constants (m, ϵ) and physical field operators. The counterterm Lagrangian for (fermion) mass renormalisation is

$$\mathcal{L}_{e,CT} = \widehat{\bar{\psi}}(x)(iA\not{\partial} - B)\widehat{\psi}(x) . \quad (39)$$

The renormalised fermion Lagrangian is thus

$$\begin{aligned} \mathcal{L}_{e,R} &= \mathcal{L}_{e,unren} + \mathcal{L}_{e,CT} \\ &= \widehat{\bar{\psi}}(x)(i(1+A)\not{\partial} - (m+B))\widehat{\psi}(x) . \end{aligned} \quad (40)$$

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

$$\begin{aligned} S_{F,vac,R}(p)^{-1} &= \not{p} \left(1 + A + \frac{\epsilon^2}{16\pi^2} \Gamma(s) \right) \\ &\quad - m \left(1 + \frac{B}{m} + \frac{\epsilon^2}{4\pi^2} \Gamma(s) \right) - \Sigma_{vac,finite}^{(1)}(p) . \end{aligned} \quad (41)$$

The obvious choice

$$A = -\frac{\epsilon^2}{16\pi^2} \Gamma(s) \quad ; \quad B = -\frac{\epsilon^2 m}{4\pi^2} \Gamma(s) \quad (42)$$

leads to a finite result, in diagrammar,

$$\text{---} \bigcirc S_{F,R} \text{---} = \text{---} \text{---} + \left[\text{---} \text{---} \text{---} + \text{---} \times \text{---} \right] + \dots$$

The additional diagram represents the counterterm contribution

$$\text{---} \times \text{---} = S_{F,vac}^{(0)}(p)[-A\not{p} + B]S_{F,vac}^{(0)}(p) . \quad (43)$$

The form invariance of the Lagrangian under this renormalisation procedure is then implemented by defining the wavefunction (actually field operator) renormalisation

$$\widehat{\psi}_{bare}(x) = [1 + A]^{1/2} \widehat{\psi}(x) \quad (44)$$

and the bare mass

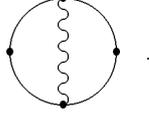
$$m_{bare} = m - \delta m \quad (45)$$

(to the given order), so that

$$\mathcal{L}_{e,R} = \widehat{\bar{\psi}}_{bare}(x)(i\not{\partial} - m_{bare})\widehat{\psi}_{bare}(x) , \quad (46)$$

that is the counterterms necessary to keep $\Sigma^{(1)}$ finite have been completely absorbed in a redefinition of the ingredients of the (free) fermion Lagrangian.

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



We shall return to some aspects of the renormalisation problem when we talk about the derivation of explicit relativistic functionals.

We then leave vacuum QED and discuss briefly the simplest relativistic many fermion problem: The **Relativistic Homogeneous Electron Gas** (RHEG). This system is characterised by a ground state that contains N electrons per volume V ,

$$n_0 = \frac{N}{V} . \quad (47)$$

The relativistic version is essentially the same model as the nonrelativistic equivalent with the difference that the kinetic energy is replaced by the relativistic form and the Coulomb interaction is replaced by the exchange of photons.

The fermion propagator reads

$$S_F(x, y) = -i \langle \phi_0 | T(\hat{\psi}(x) \hat{\bar{\psi}}(y)) | \phi_0 \rangle , \quad (48)$$

with $|\phi_0\rangle$ denoting the ground state of the RHEG. This differs from the vacuum propagator $S_{F, vac}$ already in lowest order as $S_{F, vac}$ describes free electrons and positrons while S_F of the RHEG describes electrons and positrons embedded in a medium.

The result of an explicit, straightforward evaluation can be expressed in the form

$$S_F^{(0)}(p) = S_{F, vac}^{(0)}(p) + S_{F, D}^{(0)}(p) \quad (49)$$

with

$$S_{F, D}^{(0)}(p) = 2\pi i \delta(p^0 - E_p) \frac{\not{p} + m}{2E_p} \Theta(k_F - |\underline{p}|) \quad (50)$$

$$E_p = [\underline{p}^2 + m^2]^{1/2} ; \quad k_F = [3\pi^2 n_0]^{1/3} . \quad (51)$$

The quantity in Eq.(50) is the contribution to the propagator due to finite density of real electrons. An alternative decomposition of the propagator in lowest order can be given,

$$S_F^{(0)}(p) = S_{F, -}^{(0)}(p) + S_{F, +}^{(0)}(p) . \quad (52)$$

This decomposition contains a contribution due to the electrons,

$$S_{F, +}^{(0)}(p) = \frac{(\not{p}_+ + m)}{2E_p} \left[\frac{\Theta(|\underline{p}| - k_F)}{p^0 - E_p + i\epsilon} + \frac{\Theta(k_F - |\underline{p}|)}{p^0 - E_p - i\epsilon} \right] , \quad (53)$$

with

$$p_{\pm}^{\mu} = (\pm E_p, \underline{p}) \ , \quad (54)$$

(which has some resemblance to the corresponding nonrelativistic propagator) and a positron contribution,

$$S_{F,-}^{(0)}(p) = \frac{(\not{p} - m)}{2E_p} \left(\frac{-1}{p^0 + E_p - i\epsilon} \right) \ . \quad (55)$$

The lowest order fermion propagator of the RHEG will in the following be denoted by a double line

$$S_F^{(0)}(p) = \text{---} \text{---} \text{---} \ . \quad (56)$$

The other two basic elements of perturbation theory, the free photon propagator and the simple vertex, remain unchanged. On the other hand, the full photon propagator, which in this case is given by

$$D_{\mu\nu}(x, y) = -i\epsilon^2 \langle \phi_0 | T(\hat{A}_{\mu}(x) \hat{A}_{\nu}(y)) | \phi_0 \rangle \ , \quad (57)$$

and the full vertex differ from the vacuum QED result. The reason is that not only $e^+ - e^-$ pairs screen the bare interaction but also virtual electron-hole pairs.

The discussion of the ground state energy of the RHEG is the basis of the local density approximation (LDA), as in the nonrelativistic case. We shall discuss the necessary details in connection with the explicit consideration of this limit in section 4. We shall see there that the renormalisation procedure, which is also necessary for this system, concerns essentially only the vacuum aspects involved.

In the discussion of inhomogeneous systems (like atoms, molecules etc.) the fermions have to be subjected to an additional external field, which represents the fixed nuclei and/or any other external perturbation present. In this case the original QED Lagrangian has to be supplemented by an external interaction term,

$$\mathcal{L}(x) = \mathcal{L}_{QED}(x) + \mathcal{L}_{ext}(x) \quad (58)$$

$$\mathcal{L}_{ext}(x) = -e \hat{j}^{\nu}(x) V_{\nu}(x) \ . \quad (59)$$

For the discussion of stationary systems the external four vector is static,

$$V_{\mu}(x) \equiv V_{\mu}(\underline{x}) \ . \quad (60)$$

It will be denoted in diagrammar as

$$V \longrightarrow \text{~~~~} \times \ . \quad (61)$$

One can then show (with the aid of Noether's theorem if necessary) that the corresponding energy is conserved, so that the Hamiltonian is given by

$$\hat{H} = \int d^3x \hat{T}^{00}(x) \quad (62)$$

$$= \int d^3x \hat{\psi}(x) (-i\underline{\gamma} \cdot \underline{\nabla} + m) \hat{\psi}(x) \quad (63)$$

$$\begin{aligned}
 & -\frac{1}{8\pi} \int d^3x \left\{ \partial^0 \hat{A}_\nu(x) \partial^0 \hat{A}^\nu(x) + \underline{\nabla} \hat{A}_\nu(x) \cdot \underline{\nabla} \hat{A}^\nu(x) \right\} \\
 & + e \int d^3x \hat{j}^\mu(x) \hat{A}_\mu(x) + e \int d^3x \hat{j}^\mu(x) V_\mu(\underline{x}) .
 \end{aligned}$$

The renormalised Hamiltonian has the form

$$\hat{H}_R = \hat{H} - VEV + CT , \quad (64)$$

involving the subtraction of the vacuum expectation value and the addition of counterterms analogous to the counterterms of the Lagrangian.

3 Foundations

The first topic is the extension of the Hohenberg-Kohn (HK) theorem [16] to the case of relativistic QED systems.

3.1 The relativistic Hohenberg-Kohn theorem

This extension was first formulated by Rajagopal and Callaway [17, 18] (and by MacDonald and Vosko [19]). As expected for a relativistically covariant situation, the theorem states that the ground state energy is a unique functional of the ground state four current,

$$E_0[j^\mu] = F[j^\mu] + \int d^3x j^\mu(\underline{x}) V_\mu(\underline{x}) , \quad (65)$$

with F being a universal functional of j^μ . There are, nonetheless, a number of points that should be discussed more closely.

The arguments used in the original proof are based on QED, but the question of possible divergencies was ignored. As the proof relies (as in the nonrelativistic case) on the celebrated "reductio ad absurdum", one has to make sure that well defined, finite quantities for the ground state energy and the four current are involved [20],

$$E_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle - \langle vac | \hat{H}_e + \hat{H}_\gamma + \hat{H}_{int} | vac \rangle + \Delta E_{0,CT} \quad (66)$$

$$j^\mu(\underline{x}) = \langle \Phi_0 | \hat{j}^\mu(\underline{x}) | \Phi_0 \rangle + \Delta j^\mu(\underline{x}) , \quad (67)$$

that is quantities including all vacuum subtractions and counterterms (Δ). In addition, one has to make sure that the structure of the counterterms does not invalidate the proof. With these precautions, one can establish the usual chain of unique maps

$$\left\{ V_\nu \left| V_\nu + \partial_\nu A \right. \right\} \iff \left\{ |\Phi_0\rangle \left| \text{with } |\Phi_0\rangle \text{ from } V_\nu + \partial_\nu A \right. \right\} \iff j^\nu(\underline{x}) . \quad (68)$$

There exists a one-to-one correspondence between the class of external potentials differing by a static gauge transformation and the corresponding class of ground

states. This class of physically equivalent ground states is uniquely determined by the ground state four current. As a consequence one can express all ground state observables (including the energy) as a unique functional of the ground state four current

$$O[j^\mu] = \langle \Phi_0[j^\mu] | \hat{O} | \Phi_0[j^\mu] \rangle + \Delta O - VEV . \quad (69)$$

As a side remark one may note, that both the ground state energy and the four current are gauge invariant quantities.

For the case of a purely electrostatic, external potential,

$$V^\mu(\underline{x}) = \left\{ V^0(\underline{x}), \underline{0} \right\} , \quad (70)$$

the proof can be repeated using just the zeroth component of the four current (i.e. the charge density) $j^0(\underline{x}) \equiv n(\underline{x})$ [21]. The ground state energy and all variables are then functionals of the density alone. It should be emphasised that this does not imply that the spatial components of the current vanish in this case. It only implies that the three current has to be interpreted as a functional of $n(\underline{x})$,

$$\underline{j}(\underline{x}) = \langle \Phi_0[n] | \hat{\underline{j}}(\underline{x}) | \Phi_0[n] \rangle = \underline{j}([n], \underline{x}) . \quad (71)$$

With the Ritz principle, already involved in the details of the proof of the HK theorem, one may formulate the basic variational principle of RDFT as

$$\frac{\delta}{\delta j^\nu(\underline{x})} \left\{ E_0[j^\nu] - \mu \int d^3y j^0(\underline{y}) \right\} = 0 . \quad (72)$$

The subsidiary condition implies charge (rather than number) conservation.

This variational principle is utilised directly in relativistic extended Thomas-Fermi (RETF) models [22, 23, 20], in which an approximate density functional representation of $E_0[j^\nu]$ is specified. The mainstay of applications are, however, the

3.2 Relativistic Kohn-Sham equations

The first step necessary to set up this scheme [24] is the representation of the exact four current of the interacting system in terms of auxiliary spinors [20],

$$j^\nu(\underline{x}) = j_{vac}^\nu(\underline{x}) + j_D^\nu(\underline{x}) . \quad (73)$$

The vacuum polarisation current j_{vac}^ν is given as [25]

$$j_{vac}^\nu(\underline{x}) = \frac{1}{2} \left\{ \sum_{\epsilon_k \leq -m} \bar{\varphi}_k(\underline{x}) \gamma^\nu \varphi_k(\underline{x}) - \sum_{-m < \epsilon_k} \bar{\varphi}_k(\underline{x}) \gamma^\nu \varphi_k(\underline{x}) \right\} , \quad (74)$$

where we do not specify a necessary counterterm in this equation and in the following. The current due to occupied discrete orbitals is

$$j_D^\nu(\underline{x}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \bar{\varphi}_k(\underline{x}) \gamma^\nu \varphi_k(\underline{x}) . \quad (75)$$

This result follows directly from the charge conjugation invariant form of the four current operator (which has been specified beforehand) if one considers a system of noninteracting particles.

In the same vein one defines the noninteracting kinetic energy (including a mass term)

$$T_s[j^\nu] = T_{s,vac}[j^\nu] + T_{s,D}[j^\nu] , \quad (76)$$

$$T_{s,vac}[j^\nu] = \frac{1}{2} \int d^3x \left\{ \sum_{\epsilon_k \leq -m} \bar{\varphi}_k(\underline{x}) \left[-i\underline{\gamma} \cdot \underline{\nabla} + m \right] \varphi_k(\underline{x}) \right. \\ \left. - \sum_{-m < \epsilon_k} \bar{\varphi}_k(\underline{x}) \left[-i\underline{\gamma} \cdot \underline{\nabla} + m \right] \varphi_k(\underline{x}) \right\} , \quad (77)$$

$$T_{s,D}[j^\nu] = \int d^3x \sum_{-m < \epsilon_k \leq \epsilon_F} \bar{\varphi}_k(\underline{x}) \left[-i\underline{\gamma} \cdot \underline{\nabla} + m \right] \varphi_k(\underline{x}) . \quad (78)$$

$T_{s,vac}$ is the kinetic contribution to the so-called Casimir energy [11] (again no counterterms displayed), while $T_{s,D}$ results from bound real electrons.

Adding and subtracting T_s as well as the covariant Hartree energy,

$$E_H[j^\nu] = \frac{1}{2} \int d^3x \int d^4y j^\mu(\underline{x}) D_{\mu\nu}^{(0)}(x-y) j^\nu(\underline{y}) , \quad (79)$$

for time independent currents

$$= \frac{e^2}{2} \int d^3x \int d^3y \frac{j^\nu(\underline{x}) j_\nu(\underline{y})}{|\underline{x} - \underline{y}|} , \quad (80)$$

to the total energy, one can rearrange the ground state energy as

$$E_0[j^\mu] = T_s[j^\mu] + E_{ext}[j^\mu] + E_H[j^\mu] + E_{xc}[j^\mu] , \quad (81)$$

with the exchange-correlation energy

$$E_{xc}[j^\mu] = F[j^\mu] - T_s[j^\mu] - E_H[j^\mu] \quad (82)$$

as usual.

Minimising E_0 with respect to the auxiliary orbitals leads to the most general relativistic Kohn-Sham (KS)-equations

$$\gamma^0 \left\{ -i\underline{\gamma} \cdot \underline{\nabla} + m + e\Psi(\underline{x}) + \not{v}_H(\underline{x}) + \not{v}_{xc}(\underline{x}) \right\} \varphi_k(\underline{x}) = \epsilon_k \varphi_k(\underline{x}) , \quad (83)$$

with the effective potentials

$$v_H^\nu(\underline{x}) = e^2 \int d^3y \frac{j^\nu(\underline{y})}{|\underline{x} - \underline{y}|} \quad (84)$$

$$v_{xc}^\nu(\underline{x}) = \frac{\delta E_{xc}[j^\mu]}{\delta j_\nu(\underline{x})} . \quad (85)$$

This set of equations has to be solved selfconsistently, leading in principle to the exact $j^\mu(\underline{x})$ and hence energies etc.

A glance at the ingredients of the general relativistic KS-scheme reveals a problem of considerable difficulty. For instance, the evaluation of the vacuum contributions (in j^μ and T_s) requires summation over all negative and positive energy solutions (as well as renormalisation) in each step of the selfconsistency procedure. All effective potentials involved are endowed with a Minkowski space structure.

Fortunately, for practical electronic structure calculations two approximations are possible:

1. The most important simplification arises from the **no-sea approximation**, in which all radiative corrections are neglected

$$j_{vac}^\mu = 0 \quad T_{s,vac} = 0 \quad E_{xc,vac} = 0 . \quad (86)$$

If necessary, one may evaluate these contributions perturbatively, that is after selfconsistency has been achieved without these terms. This approximation should be useful for all systems of interest, with the exception possibly of super-heavy atoms.

2. For the case that the external potential is purely **electrostatic** (a situation commonly encountered in electronic structure calculations), the charge density is the only relevant variable, for instance via

$$\tilde{E}_H[n] = E_H[n, \underline{j}[n]] \quad , \quad \tilde{E}_{xc}[n] = E_{xc}[n, \underline{j}[n]] . \quad (87)$$

As a consequence the Hartree and the xc -potentials only consist of a time-like component (rather than a four vector structure), so e.g.

$$v_H^\mu(\underline{x}) = (\tilde{v}_H(\underline{x}), \underline{0}) \quad (88)$$

with

$$\tilde{v}_H(\underline{x}) = \frac{\delta \tilde{E}_H[n]}{\delta n(\underline{x})} = \frac{\delta E_H[j^\nu]}{\delta n(\underline{x})} + \sum_k \int d^3 x' \frac{\delta E_H[j^\nu]}{\delta j^k(\underline{x}')} \frac{\delta j^k(\underline{x}')}{\delta n(\underline{x})} \quad (89)$$

as there is an explicit functional dependence of \underline{j} .

The resulting **electrostatic, no-sea KS-equations** are (all \sim are dropped)

$$\left\{ -i\alpha \cdot \nabla + \beta m + V_{ext}(\underline{x}) + v_H(\underline{x}) + v_{xc}(\underline{x}) \right\} \varphi_k(\underline{x}) = \epsilon_k \varphi_k(\underline{x}) , \quad (90)$$

where the density and the three current are given by

$$n(\underline{r}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi_k^\dagger(\underline{x}) \varphi_k(\underline{x}) \quad (91)$$

$$\underline{j}(\underline{r}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi_k^\dagger(\underline{x}) \underline{\alpha} \varphi_k(\underline{x}) . \quad (92)$$

One should note that the exact current $\underline{j}[n]$ has been replaced by the KS current $\underline{j}(\underline{r})$. The KS current is not necessarily identical with the (unknown) functional $\underline{j}[n]$, but expected to be an acceptable approximation. In any case, possible differences that arise (eg. from inserting $\underline{j}[n]$ in the transverse Hartree energy) are absorbed in a redefinition of E_{xc} .

One may also decompose the interaction mediated by the free photon propagator into a Coulomb (longitudinal) and a transverse part (as discussed before)

$$D_{\mu\nu}^{(0)}(x-y) = g_{\mu 0} g_{\nu 0} \frac{e^2}{|\underline{x}-\underline{y}|} \delta(x^0 - y^0) + D_{\mu\nu}^T(x-y) . \quad (93)$$

If one neglects the transverse part, one obtains the longitudinal limit of RDFT, which corresponds to the use of the Dirac-Coulomb Hamiltonian, a kind of standard in quantum chemistry. Inclusion of the transverse term recovers the retardation and magnetic effects, which are usually included in a weakly relativistic limit in the form of the Dirac-Coulomb-Breit (DCB) Hamiltonian.

One of the problems often encountered in the application of DFT is to ensure that selfinteraction effects contained in the Hartree term are properly cancelled by the x-energy functional. This problem can be handled if one defines the x-energy in terms of KS-orbitals. For this purpose one starts with the definition of the covariant exchange energy

$$E_x = \frac{1}{2} \int d^3x \int d^4y D_{\mu\nu}^{(0)}(x-y) \text{tr} \left[S_F(x,y) \gamma^\nu S_F(y,x) \gamma^\mu \right] . \quad (94)$$

If one evaluates the propagator in the KS-picture,

$$S_F \rightarrow S^{KS} = -i \left\{ \Theta(x^0 - y^0) \sum_{\epsilon_n > \epsilon_F} \varphi_n(\underline{x}) \bar{\varphi}_n(\underline{y}) \exp[-i\epsilon_n(x^0 - y^0)] \right. \\ \left. - \Theta(y^0 - x^0) \sum_{\epsilon_F \geq \epsilon_n} \varphi_n(\underline{x}) \bar{\varphi}_n(\underline{y}) \exp[-i\epsilon_n(x^0 - y^0)] \right\} , \quad (95)$$

and uses the Feynman gauge for the photon propagator, one obtains in the electrostatic, no-sea approximation the relativistic Fock term

$$E_x^{KS}[n] = -\frac{e^2}{2} \int d^3x \int d^3y \sum_{-m < \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\cos(\omega_{kl}|\underline{x}-\underline{y}|)}{|\underline{x}-\underline{y}|} \\ \times \bar{\varphi}_k(\underline{x}) \gamma_\mu \varphi_l(\underline{x}) \bar{\varphi}_l(\underline{y}) \gamma^\mu \varphi_k(\underline{y}) , \quad (96)$$

with

$$\omega_{kl} = |\epsilon_k - \epsilon_l| . \quad (97)$$

The functional dependence of E_x^{KS} on n arises via the functional dependence of the KS-orbitals on n . The correlation energy is then

$$E_c^{KS} = E_{xc} - E_x^{KS} . \quad (98)$$

The x -potential corresponding to E_x^{KS} can not be evaluated directly via

$$v_x^{KS}(\underline{x}) = \frac{\delta E_x^{KS}[n]}{\delta n(\underline{x})} . \quad (99)$$

In order to obtain this quantity, one has to activate the relativistic extension of the

3.3 Optimised potential method

The optimised potential method (OPM) [26, 27, 28, 29, 30, 21] relies on the fact that the functional derivative of an energy expression with respect to the density can be evaluated with the aid of the chain rule

$$\frac{\delta E}{\delta n(\underline{x})} = \sum_k \int d^3x' d^3x'' \frac{\delta E}{\delta \varphi_i(\underline{x}')} \frac{\delta \varphi_i(\underline{x}')}{\delta v_{KS}(\underline{x}'')} \frac{\delta v_{KS}(\underline{x}'')}{\delta n(\underline{x})} + c.c. , \quad (100)$$

if the dependence on the density is implicit via the orbitals. The quantity $\delta v_{KS}(\underline{x}')/\delta n(\underline{x})$ is the inverse KS response function. For the functional derivative of the orbitals with respect to the potential an explicit result can be derived from the KS equations (which also allows the direct evaluation of the KS response function)

$$\frac{\delta \varphi_k(\underline{x})}{\delta v_{KS}(\underline{y})} = -G_k(\underline{x}, \underline{y}) \varphi_k(\underline{y}) \quad (101)$$

with

$$G_k(\underline{x}, \underline{y}) = \sum_{-m < \epsilon_l < m, l \neq k} \frac{\varphi_l(\underline{x}) \varphi_l^\dagger(\underline{y})}{(\epsilon_l - \epsilon_k)} . \quad (102)$$

Finally, the functional derivative of the energy with respect to the orbitals is known if the energy is specified as $E = E[\varphi_i, \bar{\varphi}_i]$.

The standard procedure can readily be applied to the exchange term (analogous to the original derivation given by Talman and Shadwick [27]) and leads to the ROPM integral equation for the x -potential

$$\int d^3x' K(\underline{x}, \underline{x}') v_x(\underline{x}') = Q(\underline{x}) , \quad (103)$$

with

$$K(\underline{x}, \underline{x}') = \sum_{-m < \epsilon_k \leq \epsilon_F} \varphi_k^\dagger(\underline{x}) G_k(\underline{x}, \underline{x}') \varphi_k(\underline{x}') + c.c. \quad (104)$$

$$Q(\underline{x}) = \sum_{-m < \epsilon_k \leq \epsilon_F} \int d^3x' \varphi_k^\dagger(\underline{x}) G_k(\underline{x}, \underline{x}') \frac{\delta E_x^{KS}[n]}{\delta \varphi_k^\dagger(\underline{x}')} + c.c. , \quad (105)$$

which corresponds to the electrostatic, no-sea limit. A covariant extension can readily be derived.

This integral equation has to be solved selfconsistently together with the KS-orbital equations. In this fashion one establishes the functional relation between v^{KS} and n , implicitly. One advantage of the OP-method is (as advertised) the fact that selfinteraction effects are cancelled correctly. If one adjusts a trivial constant, so that

$$v_x(r \rightarrow \infty) = 0 \quad (106)$$

one finds for finite systems the asymptotic behaviour

$$v_x^{ROPM}(r \rightarrow \infty) = -\frac{1}{r} . \quad (107)$$

The OP-procedure can be applied for the full x-energy (longitudinal as well as transverse). It produces spinor solutions that do not depend on the gauge of the free photon propagator $D_{\mu\nu}^{(0)}$, justifying in retrospect the use of the Feynman gauge in the definition (By contrast gauge problems arise for the transverse, nonlocal, orbital-dependent Dirac-Fock exchange).

As the three current $\underline{j}(\underline{x})$ is a trivial functional of the orbitals and the orbitals are functionals of the density, the procedure establishes (indirectly) a functional dependence of the form

$$\underline{j}^{KS,OPM} = \underline{j}^{KS}[n] . \quad (108)$$

The selfconsistent OPM-procedure is much more involved than the direct KS-scheme. For this reason a search for some shortcuts seems mandatory. This aspect as well as a valuation of numerical results will follow later.

As a final point of this section on fundamentals, we take a brief look at the weakly relativistic limit of the theory and the connection with nonrelativistic current density functional theory [31, 32, 33].

3.4 Weakly relativistic limit

The standard weakly relativistic limit of the QED Hamiltonian can be obtained with techniques as the low order Foldy-Wouthuysen transformation or by direct expansion. The results (all constants reinstated in this case) is the Pauli-type Hamiltonian

$$\hat{H}_P = \int d^3x \hat{\varphi}^+(\underline{x}) \left\{ \frac{1}{2m} \left[(-i\hbar\nabla)^2 + 2i\hbar \frac{e}{c} \underline{V}(\underline{x}) \cdot \nabla + \frac{e^2}{c^2} \underline{V}(\underline{x})^2 \right] \right. \quad (109) \\ \left. - \frac{e\hbar}{2mc} \underline{\sigma} \cdot (\nabla \times \underline{V}(\underline{x})) + eV_0(\underline{x}) \right\} \hat{\varphi}(\underline{x}) + \hat{H}_{ee} .$$

The notation implies

- $\hat{\varphi}(\underline{x})$ is a nonrelativistic field operator with a two component structure
- $\underline{\sigma}$ are the Pauli matrices

– \hat{H}_{ee} represents the standard Coulomb interaction as the limit of the relativistic $e^- - e^-$ interaction.

For the further discussion it is relevant to note that the gauge term $\frac{e^2}{c^2} \underline{V}^2$ is of order $1/c^2$, while the other terms are at most of order $1/c$.

The weakly relativistic limit of the three current operator can be extracted with the same techniques leading to

$$\underline{\hat{j}}(\underline{x}) = \underline{\hat{j}}_p(\underline{x}) - \frac{e}{c} \underline{\nabla} \times \underline{\hat{m}}(\underline{x}) - \frac{e}{mc} \underline{V}(\underline{x}) \hat{n}(\underline{x}) . \quad (110)$$

It contains the paramagnetic current operator

$$\underline{\hat{j}}_p(\underline{x}) = -\frac{i\hbar}{2m} \left[\hat{\varphi}^+(\underline{x}) \left(\underline{\nabla} \hat{\varphi}(\underline{x}) \right) - \left(\underline{\nabla} \hat{\varphi}^+(\underline{x}) \right) \hat{\varphi}(\underline{x}) \right] , \quad (111)$$

the magnetisation-density operator

$$\underline{\hat{m}}(\underline{x}) = -\frac{e\hbar}{2mc} \hat{\varphi}^+(\underline{x}) \underline{\sigma} \hat{\varphi}(\underline{x}) , \quad (112)$$

and the standard density operator

$$\hat{n}(\underline{x}) = \hat{\varphi}^+(\underline{x}) \hat{\varphi}(\underline{x}) . \quad (113)$$

In discussing the gauge structure of the problem at hand, some difficulties seem to arise. One first notes that the Pauli Hamiltonian is invariant under the gauge transformation

$$\hat{\varphi}'(\underline{x}) = e^{-ie\lambda(\underline{x})/\hbar} \hat{\varphi}(\underline{x}) \quad ; \quad \underline{V}'(\underline{x}) = \underline{V}(\underline{x}) - c \underline{\nabla} \lambda(\underline{x}) , \quad (114)$$

that is

$$\hat{H}_P(\hat{\varphi}', \underline{V}') = H_P(\hat{\varphi}, \underline{V}) . \quad (115)$$

Concerning the currents one can state that the paramagnetic current $\underline{\hat{j}}_p(\underline{x})$ is not invariant under this gauge transformation, but the combination

$$\underline{\hat{j}}_p(\underline{x}) - \frac{e}{mc} \underline{V}(\underline{x}) \hat{n}(\underline{x}) \quad (116)$$

and hence the total nonrelativistic current $\underline{\hat{j}}(\underline{x})$ is invariant.

The problem arises if one reexpresses the Hamiltonian in terms of the (physical) current and density operators

$$\hat{H}_P = \hat{T} + \hat{H}_{ee} - \int d^3x \left\{ -\frac{e}{c} \underline{V}(\underline{x}) \cdot \underline{\hat{j}}(\underline{x}) + \left[eV_0(\underline{x}) - \frac{e^2}{2mc^2} \hat{V}^2(\underline{x}) \right] \hat{n}(\underline{x}) \right\} . \quad (117)$$

This form suggests that n and \underline{j} are the basic variables of the theory, but it is not possible to prove a HK-theorem with this Hamiltonian, establishing $E_0 = E_0[n, \underline{j}]$, which seems to contradict the statements of RDFT at first glance. The resolution of this dilemma is the fact that not all terms of order $1/c^2$ are included in \hat{H}_P , i.e. the Hamiltonian is not consistent with respect to an expansion in $1/c$. The contribution to \hat{H}_P which does not allow the proof of a HK-theorem is the gauge term $\frac{e^2}{c^2} \underline{V}^2$. This means: If one neglects all terms of the order $1/c^2$ consistently, the proof of a HK-theorem with n and \underline{j} as basic variables is possible. It remains to be investigated whether inclusion of all terms of order $1/c^2$ leads to a consistent gauge invariant result to that order.

4 Functionals

Applications of RDFT may, as in nonrelativistic DFT, either use the KS-scheme or RETF-methods. In the first instance knowledge of

$$E_{xc}[j^\mu] \quad \text{resp} \quad v_{xc}([j^\mu], \underline{x})$$

is required. For RETF-applications one needs, in addition, an explicit density functional representation of the noninteracting kinetic energy

$$T_s = T_s[j^\mu] \quad .$$

We shall start the discussion by consideration of E_{xc} . The simplest approximation for this quantity is obtained in the

4.1 Relativistic local density approximation (E_{xc})

The procedure used to establish the relativistic LDA (RLDA) is exactly the same as in the nonrelativistic case [4]. One calculates the energy density of the relativistic homogeneous electron gas (RHEG) and replaces the constant density n_0 by a locally varying density,

$$E_{xc}^{RLDA}[n] = \int d^3x \epsilon_{xc}^{RHEG}(n_0 = n(\underline{x})) \quad . \quad (118)$$

A dependence on the three current does not occur, as the spatial current vanishes for a homogeneous system

$$\underline{j}^{RHEG} = 0 \quad . \quad (119)$$

In the nonrelativistic case rather accurate Monte Carlo results [34] are available for the correlation contribution (the x-contribution can be obtained analytically). No Monte Carlo results exist in the relativistic case. This means that one has to start from scratch with the evaluation of diagrammatic contributions, as far as this is possible.

The difference compared to the nonrelativistic case is the fact that evaluation of the various contributions to ϵ_{xc}^{RHEG} is more involved in the relativistic case. We shall demonstrate some of the details for the simplest case ϵ_x^{RHEG} , which is given by (see eq.(94))

$$\epsilon_x^{RHEG} = \frac{1}{2} \int d^4y D_{\mu\nu}^{(0)}(x-y) \text{tr}[S_F^{(0)}(x-y) \gamma^\nu S_F^{(0)}(y-x) \gamma^\mu] + CT - VEV, \quad (120)$$

where the fermion propagators are the propagators of the RHEG. Going over to momentum space, one has

$$\epsilon_x^{RHEG} = \frac{1}{2} \int \frac{d^4q}{(2\pi)^4} \int \frac{d^4p}{(2\pi)^4} D_{\mu\nu}^{(0)}(q) \text{tr}[S_F^{(0)}(q-p) \gamma^\nu S_F^{(0)}(p) \gamma^\mu] \quad (121) \\ + CT - VEV \quad .$$

In diagrammar the loop integral and the VEV look like this,

$$\epsilon_x^{RHEG} = \frac{i}{2} \left[\text{Diagram 1} - \text{Diagram 2} \right] + CT. \quad (122)$$

The electron propagators in the first term decompose into a vacuum and density part. Thus the x-bubble corresponds to

$$\text{Diagram 1} = \text{Diagram 2} + \text{Diagram 3} + \text{Diagram 4} + \text{Diagram 5}.$$

Only the density-density loop gives a finite contribution. In the three remaining terms we recognise the divergent vacuum polarisation



and the selfenergy insertions

$$\text{Diagram 6} = \text{Diagram 7}.$$

The first term is cancelled by the VEV, the (identical) selfenergy subgraphs have to be renormalised by appropriate counterterms,

$$\epsilon_x^{RHEG} = \frac{i}{2} \left[2 \left\{ \text{Diagram 8} - \text{Diagram 9} \right\} + \text{Diagram 10} \right]. \quad (123)$$

The first term is thus seen to contain the renormalised vacuum-selfenergy insertion,

$$\epsilon_{x,1}^{RHEG} = -i \int \frac{d^4 p}{(2\pi)^4} \text{tr} \left[S_D^{(0)}(p) \Sigma_{vac,ren}^{(1)}(p) \right]. \quad (124)$$

This term vanishes for the following reason. The propagator $S_D(p)$ contains the factor $(\not{p} + m)$ and the renormalised selfenergy insertion satisfies the on-shell condition

$$\left[(\not{p} + m) \Sigma_{vac,ren}^{(1)}(p) \right]_{p^2=m^2} = 0. \quad (125)$$

Thus only the finite density-density term remains. All vacuum corrections have been eliminated by the standard renormalisation scheme. The remaining term

$$\epsilon_{x,2}^{RHEG} \equiv \epsilon_x^{RHEG} = \frac{1}{2} \int \frac{d^4 p}{(2\pi)^4} \frac{d^4 q}{(2\pi)^4} D_{\mu\nu}^{(0)}(q) \text{tr} \left\{ S_{F,D}^{(0)}(q-p) \gamma^\mu S_{F,D}^{(0)}(p) \gamma^\mu \right\} \quad (126)$$

can be evaluated in a straightforward manner [35, 36, 37], giving

$$\epsilon_x^{RHEG} = \left[-\frac{\epsilon^2}{4\pi^3} k_F^4 \right] \Phi_x(\beta) \quad (127)$$

$$\Phi_x(\beta) = 1 - \frac{3}{2} \left[\frac{\eta}{\beta} - \frac{1}{\beta^2} \operatorname{arsinh}(\beta) \right]^2 \quad (128)$$

$$\beta = \frac{(3\pi^2 n_0)^{1/3}}{m} = \frac{k_F}{m}, \quad \eta = (1 + \beta^2)^{1/2}. \quad (129)$$

Using the decomposition of the photon propagator into a longitudinal and a transverse part, one can split ϵ_x^{RHEG} into corresponding contributions [38],

$$\Phi_x^L(\beta) = \frac{5}{6} + \frac{1}{3\beta^2} + \frac{2\eta}{3\beta} \operatorname{arsinh}(\beta) - \frac{2\eta^4}{3\beta^4} \ln(\eta) - \frac{1}{2} \left(\frac{\eta}{\beta} - \frac{\operatorname{arsinh}(\beta)}{\beta^2} \right)^2 \quad (130)$$

$$\Phi_x^T(\beta) = \frac{1}{6} - \frac{1}{3\beta^2} - \frac{2\eta}{3\beta} \operatorname{arsinh}(\beta) + \frac{2\eta^4}{3\beta^4} \ln(\eta) - \left(\frac{\eta}{\beta} - \frac{\operatorname{arsinh}(\beta)}{\beta^2} \right)^2. \quad (131)$$

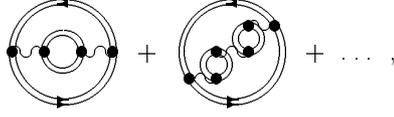
The variation of the relativistic correction factors is illustrated in Fig.4.1 of [6]. One finds that the longitudinal part does not differ very much from the nonrelativistic limit. The transverse correction factor is negative and small for low densities. It grows, however, sufficiently in magnitude so that the total x-energy density changes sign at about $\beta = 2.4$. As for instance the maximal density in Hg amounts to $\beta \approx 3$, one realizes that relativistic effects should be relevant for the inner shells of atoms.

One may look a bit more closely at the transverse part. It can either be decomposed into a magnetic and a retardation contribution or one may consider expansion in the weakly relativistic limit, giving the Breit contribution. One then finds that retardation and magnetic effects have opposite signs, the latter is dominant though. The Breit limit reproduces the exact transverse correction factor over the full range of density values of interest quite closely.

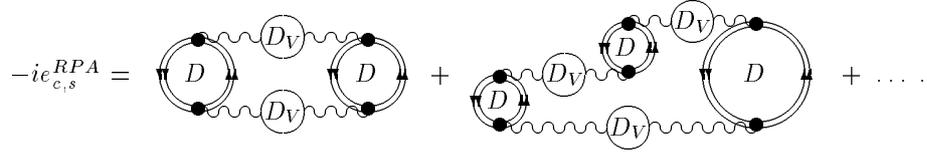
The calculation (including the renormalisation) becomes more involved if one addresses correlation contributions. As a matter of fact the only correlation contribution that has been evaluated is the relativistic random phase approximation (RPA) [35, 37, 39, 40]. It corresponds to the following diagrams,

$$-i\epsilon_{xc}^{RPA} = \begin{array}{c} \begin{array}{c} \text{Diagram 1} \\ \text{Diagram 2} \end{array} + \begin{array}{c} \text{Diagram 3} \\ \text{Diagram 4} \end{array} + \dots \\ - \begin{array}{c} \text{Diagram 5} \\ \text{Diagram 6} \end{array} - \dots + CT, \end{array}$$

where the vacuum subtraction and the fact that counterterms are necessary has been indicated. Just to illustrate the diagrammatic games, we give an alternative representation of the diagrams



which indicates that the RPA corresponds essentially to an exchange type term, in which the free propagator (that is the free interaction) is replaced by a specifically screened interaction. We will not go through the messy details of further processing the corresponding equations, but rather look at an indication of the final result in diagrammar,



Here the D in the electron loops indicate that only the electron gas part has to be inserted there

$$\text{Loop with } D = \Pi_{\mu\nu,D}^{(0)}(q) = \text{Loop with } D + \text{Loop with } D + \text{Loop with } D \dots$$

The wiggly line with D_V is the full vacuum photon propagator

$$D_{\mu\nu,V}(q)_{ren} = g_{\mu\nu} D_V(q)_{ren} \quad (\text{in Feynman gauge}) \quad (132)$$

with

$$D_V(q)_{ren} = \frac{D_V^{(0)}(q)}{1 - D_V^{(0)}(q)\Pi_{vac}(q)_{ren}} \quad (133)$$

The series of RPA-subdiagrams can be resummed [35, 37, 41] leading to a structure of the form

$$e_c^{RPA} \propto \int \frac{d^4p}{(2\pi)^4} \left\{ \ln[1 \pm D\Pi] \pm D\Pi \right\} \quad (134)$$

for both the longitudinal and transverse contributions. These integrals have only been evaluated in some approximations. In the **no-sea** approximation the full photon propagator is replaced by the free propagator,

$$D_{vac}(q)_{ren} \longrightarrow D^{(0)}(q) \quad .$$

In the no-pair approximation (corresponding to the standard procedure in quantum chemistry) one also uses the free photon propagator and evaluates in addition the polarisation insertion as

$$\Pi^{(0)}(q)_{no-pair} = + \text{[diagram: a circle with two vertices and a photon line inside]} + , \quad (135)$$

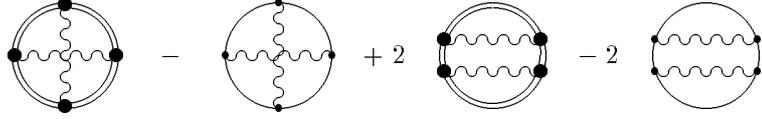
with the electron propagator on the basis of the decomposition (52). Thus in both cases one neglects the screening effects due to the vacuum. In addition, there is a (slight) difference in results due to the different evaluation of the polarisation insertion [42].

Even with these approximations the final result can only be obtained numerically. Writing the longitudinal as well as the transverse contribution of the no-sea result in the form

$$e_c^{RPA}(n_0) = \left\{ e_c^{RPA}(n_0) \right\}_{nonrel} \Phi_c^{RPA}(\beta) , \quad (136)$$

one finds that the correction factors can, as in the case of exchange, can be quite substantial for higher densities [6].

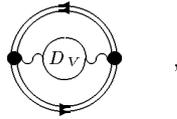
Further diagrams have not been evaluated for the relativistic homogeneous electron gas, but a number of high density limits are available. To second order (e^4) two additional correlation diagrams contribute,



Both diagrams require renormalisation beyond the vacuum subtraction indicated. In the high density limit one finds [43] for their total contribution,

$$e_c^{(2)}(n_0) \xrightarrow{\beta \gg 1} \frac{e^4}{12\pi^4} k_F^4 \left(-3.18 \pm 0.12 \right) . \quad (137)$$

In addition the two loop contribution to the screened exchange [43],



which is not contained in the no-sea approximation, can also be calculated in this limit,

$$e_x^{(2)}(n_0) \xrightarrow{\beta \gg 1} \frac{e^4}{12\pi^4} k_F^4 \left(\ln(2\beta) - \frac{11}{6} \right) . \quad (138)$$

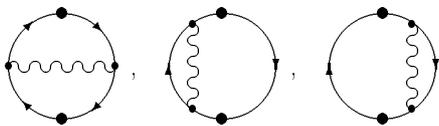
By comparison, for the no-sea RPA-result one has [35, 37]

$$e_c^{RPA}(n_0) \xrightarrow{\beta \gg 1} \frac{e^4}{12\pi^4} k_F^4 \left(-7.796 \right) . \quad (139)$$

One notes that in the limit considered, the additional second order contributions amount to about 40% of the RPA value and that in the extreme high density limit the screened exchange contribution eventually dominates over all other known contributions. This occurs, however, only for $\beta \approx 10^3$, which is not relevant for electronic structure calculations.

4.2 Relativistic generalised gradient approximation (E_{xc})

As the x and RPA correlation contributions in LDA are known not to yield optimal results (for atoms and other systems) in the nonrelativistic case, one has to consider improvements. The next step (thinking of the history for nonrelativistic systems) would be direct gradient expansions [44, 45, 46, 47, 48, 49, 50, 51]. The problem is, that the corresponding contributions as e.g.



of the homogeneous electron gas are difficult to evaluate (and have not been evaluated) for relativistic systems. In addition, they have not been found to be very accurate in the nonrelativistic regime. In order to make some headway, we have carried through the following scheme [52, 53]:

For the x -part

Step 1: Solve the KS-OPM problem for a selection of atoms with closed subshells (17 atoms were chosen).

Step 2: Use the results to set up a semiempirical relativistic generalised gradient approximation (GGA), relying on the form

$$E_{x,rel}^{GGA}[n] = \int d^3x e_x^{LDA}(n) [\Phi_{x,0}(\beta) + g(\xi)\Phi_{x,2}(\beta)] . \quad (140)$$

For the function g of the dimensionless density gradient

$$\xi = (\nabla n)^2 / [4n^2(3\pi^2 n)^{2/3}] \quad (141)$$

we choose nonrelativistic GGA forms. We used the Becke 88 [54], the Engel-Chevary-Macdonald-Vosko 92 [55] and the Perdew-Wang 91 [56] forms and found that final results for E_x only varied marginally with $g(\xi)$. The function $\Phi_{x,0}$ is the LDA relativistic correction factor indicated earlier. For the relativistic correction factor $\Phi_{x,2}$ we choose a reasonably flexible ansatz in the form of a [2/2] Padé-approximant,

$$\Phi_{x,2}(\beta) = \frac{a_0 + a_1\beta^2 + a_2\beta^4}{1 + b_1\beta^2 + b_2\beta^4} . \quad (142)$$

The form can be used for both the longitudinal and the transverse contributions, if one sets

$$a_0^L = 1 \quad a_0^T = 0 \quad , \quad (143)$$

which guarantees that the correct weakly relativistic limit is obtained. The fact that $\Phi_{x,2}$ must be an even function of β follows from the time reversal invariance.

Step 3: The coefficients have been fitted to the exact relativistic correction to the longitudinal exchange energy,

$$\Delta E_x^L = E_{x,rel}^L[n_{rel}] - E_{x,nrel}[n_{nrel}] \quad , \quad (144)$$

and the exact transverse exchange energy $E_{x,rel}^T[n_{rel}]$, with all quantities being obtained by corresponding ROPM calculations. Explicit results, indicating their quality, will be shown in Section 5. For the moment we look at an illustration of

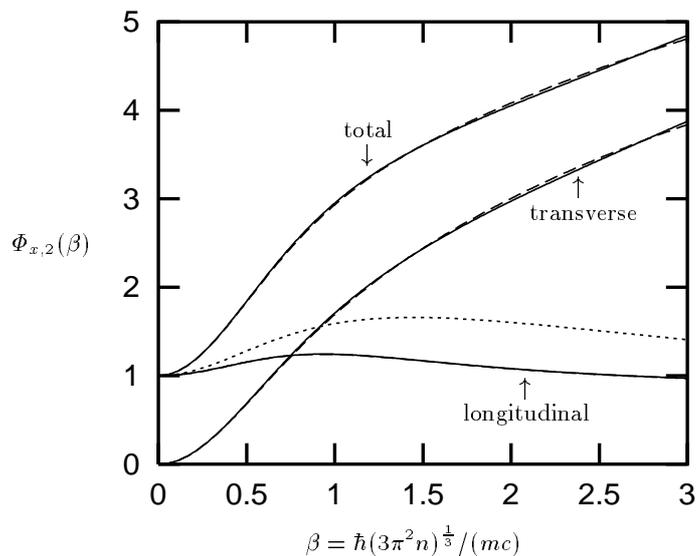


Fig. 1. Relativistic correction factors for the gradient contribution to the exchange energy density for both ECMV92 (solid line) and B88 (long dashes). Also shown is the relativistic correction factor for the second order gradient correction for $T_s[n]$ (short dashes).

the correction factors for the B88 and ECMV92 GGAs (Fig.1) and an abbreviated comparison of the constants in the Padé-ansatz for various GGA functionals and the longitudinal term:

Functional	a_1^L	a_2^L	b_1^L	b_2^L
B88 [54]	2.209	0.669	1.331	0.795
ECMV92 [55]	2.213	0.669	1.330	0.795
PW91 [56]	2.216	0.670	1.327	0.794

It remains to be stated that we also used other Padé-forms (eg. [3/3]) without finding significant improvements.

For the case of the **correlation term** basic data are hard to come by. In this case a more global form [53],

$$E_{c,rel}^{GGA}[n] = \int d^3x e_{c,nrel}^{GGA}(n, (\nabla n)^2, \dots) \Phi_c(\beta) \quad (145)$$

has been fitted to second order perturbation theory results (on the basis of a Dirac-Coulomb-Breit Hamiltonian) for the Neon isoelectronic series [57], as it seemed to be the most systematic set of quantum chemical data available. For the nonrelativistic GGA the Perdew-Wang 91 [56] and the Lee-Yang-Parr [58] forms have been used, Φ_c is again a [2/2] Padé-approximant. The fitting procedure used

$$\Delta E_c = E_{c,rel}[n_{rel}] - E_{c,nrel}[n_{nrel}] \quad (146)$$

as before, in order to suppress errors in the individual energy values as much as possible.

The last functional to be discussed is the

4.3 Relativistic gradient expansion for $T_s[n]$

As already indicated, this functional is of interest for RETF-applications. We discuss it for two reasons. First, it provides another example for the need of renormalisation. Second, the results exhibit a certain amount of physics [59, 22].

The starting point of the discussion is the definition of the exact kinetic energy and the exact current in terms of the exact fermion propagator

$$T[j^\mu] = -i \int d^3x \lim_s \operatorname{tr} \left[\left(-i \underline{\gamma} \cdot \underline{\nabla} + m \right) S_F(x, y) \right] - VEV + CT \quad (147)$$

$$j^\mu(\underline{x}) = -i \lim_s \operatorname{tr} \left[S_F(x, y) \gamma^\nu \right] - VEV + CT \quad (148)$$

The symmetric limit indicated is defined as

$$\lim_s \equiv \frac{1}{2} \left(\lim_{y \rightarrow x, y^0 > x^0} + \lim_{y \rightarrow x, y^0 < x^0} \right) \Big|_{(x-y)^2 \geq 0} \quad (149)$$

It is the relativistic equivalent of the nonrelativistic limit

$$\lim_{\underline{y} \rightarrow \underline{x}} \lim_{t_y \rightarrow t_x^+} \quad .$$

The definitions given are quite general. In order to arrive at the noninteracting situation, one has to replace the exact fermion propagator by the KS propagator, which can be specified alternatively by the differential equation [60]

$$(i\cancel{\partial}_x - m - \cancel{\psi}_{KS}(\underline{x})) S_F^{KS}(x, y) = \delta^{(4)}(x - y) . \quad (150)$$

The standard perturbation expansion of this propagator in powers of the potential can be indicated in diagrammar as

$$KS = \begin{array}{c} \parallel \\ \parallel \end{array} + \begin{array}{c} \parallel \\ \bullet \\ \parallel \end{array} \text{---} \text{wavy} \times + \begin{array}{c} \parallel \\ \bullet \\ \bullet \\ \parallel \end{array} \begin{array}{c} \text{---} \text{wavy} \times \\ \text{---} \text{wavy} \times \end{array} + \dots$$

We have seen the explicit form in terms of KS-orbitals before. Renormalisation is not necessary.

The symmetric limit required for the calculation of T_s and j_μ corresponds to closing the ends of the fermion lines, after supplying them with the required weight, that is

$$\begin{aligned} -ij_\mu &= \begin{array}{c} \bullet \\ \circlearrowleft \\ \bullet \end{array} + \begin{array}{c} \bullet \\ \circlearrowleft \\ \bullet \end{array} \text{---} \text{wavy} \times + \begin{array}{c} \bullet \\ \bullet \\ \circlearrowleft \\ \bullet \\ \bullet \end{array} \begin{array}{c} \text{---} \text{wavy} \times \\ \text{---} \text{wavy} \times \end{array} + \dots - VEV + CT \\ -iT_s &= \int d^3x \left\{ \begin{array}{c} \bullet \\ \circlearrowleft \\ \bullet \end{array} + \begin{array}{c} \bullet \\ \circlearrowleft \\ \bullet \end{array} \text{---} \text{wavy} \times + \begin{array}{c} \bullet \\ \bullet \\ \circlearrowleft \\ \bullet \\ \bullet \end{array} \begin{array}{c} \text{---} \text{wavy} \times \\ \text{---} \text{wavy} \times \end{array} + \dots \right\} \\ &\quad - VEV + CT . \end{aligned}$$

We recognise outermost loops (integration), which introduce, as in standard QED without external fields, UV-divergencies. It does not make any difference whether the virtual electron-positron pairs involved in the loops are generated by the photon field or by an external potential. As a consequence the renormalisation procedure is the same as the procedure that one uses for the renormalisation of the propagators of vacuum QED. A quick inspection for j^μ shows that only the second diagram on the right-hand side is divergent. For the vacuum four current all contributions with an odd number of vertex points in the loop vanish due to Furry's theorem. From the remaining diagrams,

$$\begin{array}{c} \bullet \\ \circlearrowleft \\ \bullet \end{array} \text{---} \text{wavy} \times + \begin{array}{c} \bullet \\ \bullet \\ \circlearrowleft \\ \bullet \\ \bullet \end{array} \begin{array}{c} \text{---} \text{wavy} \times \\ \text{---} \text{wavy} \times \\ \text{---} \text{wavy} \times \end{array} + \dots ,$$

only the first one needs to be renormalised.

To see how this works, one has to evaluate T_S and j_μ explicitly. We do this using a semiclassical gradient expansion as a first step.

In order to obtain the semiclassical gradient expansion (an expansion in terms of derivatives of the effective KS-potential) one solves the differential equation for the propagator explicitly by iteration [60]. The general ansatz for the iteration is the expansion (dropping the index KS)

$$S_F(x, y) = e^{-i(x-y) \cdot v(\underline{x})} \int \frac{d^4 p}{(2\pi)^4} e^{-ip(x-y)} \sum_{k=0}^{\infty} S_F^{[k]}(p_\mu, v_\mu(\underline{x})) . \quad (151)$$

The index $[k]$ denotes the order of the potential gradients involved. Insertion of the ansatz into the differential equation yields the recursion

$$(\not{p} - m) S_F^{[k]}(p_\mu, v_\mu(\underline{x})) = \left[(i\not{\partial} v_\mu(\underline{x})) \frac{\partial}{\partial p_\mu} - i\not{\partial} \right] S_F^{[k-1]}(p_\mu, v_\mu(\underline{x})) . \quad (152)$$

The starting point for the recursion is the solution of the differential equation for a constant potential,

$$S_F^{[0]}(p_\mu, v_\mu) = S_{F, vac}^{[0]}(p) - 2\pi i \frac{(\not{p} + m)}{2E} \delta(p^0 - E) \Theta(\epsilon_F - v^0 - p^0) \Big|_{v_0=v_0(\underline{x})} . \quad (153)$$

As an example of the explicit results at this level, we look at the second order semiclassical gradient expansion of the density n and the kinetic energy density t_s for the case of a purely electrostatic external potential $v^\mu = (v^0, \underline{0})$,

$$\tilde{n}[v_0]_{reg} = \frac{p^3}{3\pi^2} + \frac{1}{12\pi^2} \Gamma\left(2 - \frac{d}{2}\right) (\nabla^2 v_0) \quad (154)$$

$$- \frac{1}{12\pi^2} \left\{ \left[\frac{E}{p} + 2 \operatorname{arsinh}\left(\frac{p}{m}\right) \right] (\nabla^2 v_0) + \left[\frac{E^2}{p^2} - 3 \right] \frac{(\nabla v_0)^2}{2p} \right\}$$

$$\tilde{t}_s[v_0]_{reg} = \frac{m^4}{16\pi^2} \Gamma\left(2 - \frac{d}{2}\right) + \frac{1}{8\pi^2} \left\{ pE^3 + p^3E - \operatorname{arsinh}\left(\frac{p}{m}\right) \right\} \quad (155)$$

$$+ \frac{1}{24\pi^2} \Gamma\left(2 - \frac{d}{2}\right) (\nabla v_0)^2 - \frac{1}{12\pi^2} \left[\frac{E^2}{p} + p \right] (\nabla^2 v_0)$$

$$- \frac{1}{12\pi^2} \left[\frac{E^3}{2p^3} - \frac{E}{p} + \operatorname{arsinh}\left(\frac{p}{m}\right) \right] (\nabla v_0)^2 ,$$

where

$$E = \epsilon_F - v_0(\underline{x}) \quad ; \quad p = \sqrt{E^2 - m^2} \Theta(E^2 - m^2) . \quad (156)$$

The results have been obtained with dimensional regularisation. One recognises contributions which diverge in the limit $d \rightarrow 4$. There is a divergent contribution

to the kinetic energy due to the Dirac-sea, which is removed by vacuum energy subtraction

$$\langle vac | \hat{H}_e | vac \rangle = \frac{m^4}{16\pi^2} \Gamma\left(2 - \frac{d}{2}\right) . \quad (157)$$

The UV divergencies (proportional to Δv_0) are removed by the same counter-terms which are the lowest order contribution to the vacuum polarisation insertion in standard QED without external fields.

After renormalisation has been carried out, one has finite (in the limit $d \rightarrow 4$) expressions of the form

$$j^\nu(\underline{x}) = j^\nu(v_\mu(\underline{x}), \underline{\nabla}v_\mu(\underline{x}), \dots) \quad (158)$$

$$t_s(\underline{x}) = t_s(v_\mu(\underline{x}), \underline{\nabla}v_\mu(\underline{x}), \dots) . \quad (159)$$

The last step is the derivation of a current (or density in the electrostatic case) gradient expansion. This is obtained by order by order inversion of the first relation

$$v_\mu(\underline{x}) = v_\mu(j^\nu(\underline{x}), \underline{\nabla}j^\nu(\underline{x}), \dots) \quad (160)$$

and insertion into the second relation.

We first give the results for the case of an electrostatic external potential to the fourth order

$$T_s^{RGE0}[n] = \int d^3x \frac{(3\pi^2 n)^{5/3}}{10\pi^2 m} \frac{10}{\beta^5} \left[\frac{1}{8} (\beta\eta^3 + \beta^3\eta - \text{arsinh}(\beta)) - \frac{1}{3}\beta^3 \right] \quad (161)$$

$$T_s^{RGE2}[n] = \frac{1}{72m} \int d^3x \frac{(\underline{\nabla}n)^2}{n} \frac{1}{\eta} \left[1 + 2\frac{\beta}{\eta} \text{arsinh}(\beta) \right] \quad (162)$$

$$T_s^{RGE4}[n] = \int d^3x \left[t_{s,V}^{RGE4}[n] + t_{s,D}^{RGE4}[n] \right] \quad (163)$$

$$t_{s,V}^{RGE4} = \frac{1}{360\pi^2} \left\{ 3\frac{\beta^2}{\eta^2} (\underline{\nabla}^2\beta)^2 + 6\frac{\beta}{\eta^4} (\underline{\nabla}^2\beta) (\underline{\nabla}\beta)^2 + \frac{3 - \beta^4\eta^2}{\eta^6} (\underline{\nabla}\beta)^4 \right\}$$

$$\begin{aligned} t_{s,D}^{RGE4} = \frac{1}{5760\pi^2} \left\{ 4\frac{(\underline{\nabla}^2\beta)^2}{\beta\eta} \left[3(1 - 4\beta^2) + 5\left(1 + 2\frac{\beta}{\eta} \text{arsinh}(\beta)\right)^2 \right] \right. \\ \left. + 2\frac{(\underline{\nabla}^2\beta)(\underline{\nabla}\beta)^2}{\beta^2\eta^3} \left[-41\beta^2 + 20\left(1 + 2\frac{\beta}{\eta} \text{arsinh}(\beta)\right) \right] \right. \\ \left. \times \left(\frac{\beta^2 + \eta^2}{2} + 2\frac{\beta}{\eta} \text{arsinh}(\beta) \right) \right] \\ \left. + \frac{(\underline{\nabla}\beta)^4}{\beta^3\eta^5} \left[3 - 19\beta^2 - 8\beta^4 + 8\beta^6 + 16\beta^8 \right. \right. \\ \left. \left. + 20\left(\frac{\beta^2 + \eta^2}{2} + 2\frac{\beta}{\eta} \text{arsinh}(\beta) \right)^2 \right] \right\} , \end{aligned}$$

and offer the following comments

- i The zeroth order contribution to the kinetic energy density is the TF (relativistic homogeneous electron gas) result, already obtained by Vallarta and Rosen in 1932 [61].
- ii The second and fourth order terms were only obtained in 1987 [22] and 1991 [62]. While the results for the second order term are quite compact, the result for the fourth order term looks somewhat messy. It contains explicit radiative corrections ($t_{s,vac}^{(4)}$), which correspond exactly to the Euler-Heisenberg energy (for the case of an electrostatic potential).
- iii The relativistic results go, for small value of β , over into the corresponding nonrelativistic results [63, 64].
- iv An illustration of the relativistic correction can readily be given for the zeroth and the second order. In this case the ratio $t_{s,rel}^{[k]}/t_{s,nonrel}^{[k]}$ is a function of β alone. As in the case of exchange and correlation the relativistic corrections are noticeable, especially for the case of $t_s^{[2]}$ (see Fig.1).
- v The same technique can be applied to the generation of a current gradient expansion for the case of a full four potential [65]. Obviously, there are no zeroth order current terms (they vanish in a homogeneous system). The current contribution to $t_s^{[2]}$ has the form ($\beta = (3\pi^2 n)^{1/3}/m$)

$$T_s^{RGE2}[n, \underline{j}] = \frac{3}{16} \int d^3x \frac{1}{\text{arsinh}(\beta(\underline{x}))} \quad (164)$$

$$\times \int d^3y \int d^3z \sum_{k,l=1}^3 \frac{\partial_k^y j^l(\underline{y}) \partial_k^z j^l(\underline{z}) - \partial_k^y j^l(\underline{y}) \partial_l^z j^k(\underline{z})}{|\underline{x} - \underline{y}| |\underline{x} - \underline{z}|}.$$

As we will not discuss applications of the RETF model [23, 66] in the following, we offer one brief remark at this point. The model is given by

$$E_0^{[2K]} = \sum_{i=0}^K T_S^{[2i]}[n] + E_{ext}[n] + E_H[n] + E_x^{LDA}[n] \quad (165)$$

and often combined with a spherical average of the system. Evaluation of the direct variational equations reproduces the gross features of atoms, but does not reproduce quantal effects like the shell structure. As the model does not involve correlation contributions comparison with Dirac-Fock-Slater results is adequate. The results show that the accuracy that can be obtained in the relativistic case is comparable to the accuracy in the nonrelativistic case.

5 Applications to atoms

A standard approach to relativistic Coulomb problems is the Dirac-Fock-Slater (DFS) approximation, in which the kinetic energy is treated fully in terms of relativity, while the nonrelativistic x-only LDA is used for the exchange-correlation energy. There are few investigations that use the relativistic LDA exchange functional and only a scatter addressing relativistic correlation effects

(see eg. [19, 67, 38, 68, 69, 70, 21, 71, 72]). In view of this state of affairs we set ourselves as a first goal a more detailed investigation of the quality of the RLDA functionals that are available.

We begin, however, by looking at **ROPM-results** in the x-only approximation [21] in order to assess relativistic effects in a more global fashion. Table 1

Table 1. Longitudinal ground state energies ($-E_{tot}^L$) and highest occupied eigenvalues ($-\epsilon_{mk}^L$) for closed subshell atoms from nonrelativistic OPM (NROPM [73]), relativistic OPM (ROPM [21]) and relativistic HF (RHF [8]) calculations [74] (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

shows ground state energies for neutral, spherical (that is closed subshell) atoms in the *no-sea/longitudinal* approximation. We concentrate on the first three columns, in which nonrelativistic OPM-, relativistic OPM- and relativistic HF-results can be compared. One notes that for heavier atoms

- (a) relativistic effects are obviously important,
- (b) ROPM- and RHF-results agree quite closely.

As a specific example for comparison we will use the Hg atom (here and in the following). For this atom the relativistic contribution to the total ground state energy (in the approximation specified) amounts to

$$\Delta E_{tot,1}^L = E_{tot}^{L,ROPM} - E_{tot}^{NROPM} = -1240.5 \text{hartree} ,$$

while the energy difference for the two relativistic theories is

$$\Delta E_{tot,2}^L = E_{tot}^{L,RHF} - E_{tot}^{L,ROPM} = -39mhartree .$$

This clearly establishes the need for a relativistic treatment of heavier atoms and shows that the ROPM gives an adequate representation of exchange effects. The fact that ROPM results are always slightly higher than RHF-energies can be understood on the basis of the reduced variational freedom of the ROPM orbitals.

The trends indicated are also found for the orbital energies of the highest occupied orbitals (see Table 1). The relativistic $6s_{1/2}$ -orbital in Hg is more bound by

$$\Delta\epsilon_{6s_{1/2}} = \epsilon_{6s_{1/2}}^{L,ROPM} - \epsilon_{6s_{1/2}}^{NROPM} = -67mhartree = -1.8eV ,$$

while there is little difference between the RHF and ROPM orbital energies. The last statement might imply that the orbital energies are the same for all ROPM and RHF orbitals. Table 2 (for Hg) demonstrates that this is not the case. Although the total energies agree quite closely for ROPM and RHF (and we shall see in a moment that this statement also applies to the individual contributions to E_{tot}), one finds eg.

$$\epsilon_{1s_{1/2}}^{L,RHF} - \epsilon_{1s_{1/2}}^{L,ROPM} = -26.80hartree .$$

This difference is (as expected) much smaller than the relativistic corrections to the inner orbital energies

$$\Delta\epsilon_{1s_{1/2}} = \epsilon_{1s_{1/2}}^{L,ROPM} - \epsilon_{1s_{1/2}}^{NROPM} = -290.51hartree ,$$

which corresponds to a decrease of about 10.5 %. The percentage change of the outer orbital is still very large (25.6% for the $6s_{1/2}$ orbital). These results demonstrate that it is dangerous to attach too close a physical interpretation to the orbitals and their energies.

Table 3 shows the longitudinal x-contribution to the total energy in various approximations [21, 6]. For this quantity the relativistic correction in Hg amounts to

$$\Delta E_{x,1}^L = E_x^{L,ROPM} - E_x^{NROPM} = -19.96hartree ,$$

which is still quite substantial. Comparison with the difference in the total energy indicates, however, that kinetic and direct potential effects constitute about 98% of the total relativistic effect. The difference between ROPM- and RHF-results is again fairly small

$$\Delta E_{x,2}^L = E_x^{L,RHF} - E_x^{L,ROPM} = -74mhartree .$$

Also included in Table 3 are DFS results. From the difference

$$\Delta E_{x,3}^L = E_x^{L,RHF} - E_x^{DFS} = -10.98hartree$$

Table 2. Single particle energies ($-c_{nl}^L$) for Hg from NROPM-, ROPM- and RHF-calculations in comparison with DFS-, and RLDA-results (longitudinal limit, all energies are in *hartree*).

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

one can infer (in comparison with the difference between the relativistic and the nonrelativistic results), that insertion of a relativistic density into a nonrelativistic x-functional corrects the deviation from the full relativistic result somewhat.

We now look at **RLDA-results**, first again for the case of x-only (Table 4). In the longitudinal limit, the error of the RLDA for the total energy is only of the order of 0.1% for the heavier systems (17.20*hartree* for Hg). If one compares this with the error in the x-contribution, one finds that this error is solely due to exchange

$$\Delta E_x^L = E_x^{L,ROPM} - E_x^{L,RLDA} = -17.59\textit{hartree} ,$$

which amounts to about 5%. Compared to nonrelativistic systems, this shows that the relative error of the longitudinal exchange energy is comparable (Be 14.5%, Kr 6.1%), so that the LDA-exchange contribution can as well not be considered to be sufficiently accurate in the relativistic case.

In Table 5 we look at results obtained for the full relativistic x-functional. We first note that inclusion of the transverse contribution leads to a higher ground

Table 3. Longitudinal (Coulomb) x -only energies ($-E_x^L$) for closed subshell atoms from NROPM-, ROPM-, RHF-, DFS-, and RLDA-calculations [21, 74] (all energies are in *hartree*).

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

state energy

$$\Delta E_{tot} = E_{tot}^{L,ROPM} - E_{tot}^{L+T,ROPM} = -22.12 \text{hartree} .$$

This is in accord with the fact, that the transverse term has an opposite sign with respect to the longitudinal term. The absolute error of the total RLDA-energy has, however, changed to 29.16hartree , an increase by 11.96hartree with respect to the longitudinal limit. The error in the transverse exchange energy is (see Table 6)

$$\Delta E_x^T = E_x^{T,ROPM} - E_x^{T,RLDA} = +22.17 - 34.20 = -12.03 \text{hartree} ,$$

which corresponds to a relative error slightly larger than 50%. Obviously, there is substantial room for improvement.

We next look at the correlation contribution in the LDA. As the correlation contribution in heavier atoms in LDA amounts to about 10hartree , with a relativistic correction of the order of 0.5hartree , there is hardly any difference if one performs a variational x -only calculation and evaluates the correlation-contribution with the resulting density or if one performs a more complete vari-

Table 4. Longitudinal x-only ground state energies: Selfconsistent ROPM, RHF, RLDA and RGGA results for neutral atoms with closed subshells (in *hartree* [74]).

Atom	$-E_{tot}^L$	$E_{tot}^L - E_{tot}^{L,ROPM}$		
	ROPM	RHF	RLDA	RPW91
He	2.862	0.000	0.138	0.006
Be	14.575	-0.001	0.350	0.018
Ne	128.690	-0.002	1.062	-0.024
Mg	199.932	-0.003	1.376	-0.001
Ar	528.678	-0.005	2.341	0.041
Ca	679.704	-0.006	2.656	0.026
Zn	1794.598	-0.014	4.140	-0.262
Kr	2788.848	-0.013	5.565	-0.021
Sr	3178.067	-0.013	5.996	-0.008
Pd	5044.384	-0.016	7.707	-0.067
Cd	5593.299	-0.020	8.213	-0.033
Xe	7446.876	-0.019	9.800	0.085
Ba	8135.625	-0.019	10.289	0.059
Yb	14067.621	-0.048	13.272	-0.893
Hg	19648.826	-0.039	17.204	-0.250
Rn	23601.969	-0.035	19.677	0.004
Ra	25028.027	-0.034	20.460	-0.006

ational calculation. As the RPA limit is known not to be an accurate approximation to the correlation energy, we suggest to use [21]

$$E_c^{RLDA}[n] = E_{c,rel}^{RPA}[n] - E_{c,nonrel}^{RPA}[n] + E_{c,nonrel}^{LDA}[n] . \quad (166)$$

We use only the relativistic correction to the RPA, which is added to a complete nonrelativistic functional (eg. LDA from Monte Carlo [76]). For high densities the RPA contribution in the two nonrelativistic terms cancel, so that the correlation energy is given by the relativistic RPA plus the nonrelativistic second order exchange graph. For low densities the first two terms cancel, so that the correlation energy is given by the more adequate nonrelativistic result.

One problem that one encounters for heavier elements, is the fact that experimental total energies (and hence experimental correlation energies) are not available. (It is difficult to measure successive ionisation energies of all positive ions for heavier systems.) Thus we compare LDA-results with results obtained in second order many-body perturbation theory (MBPT) [57]. Table 7 illustrates the well-known fact that nonrelativistic LDA correlation energies overestimate the correct values by a factor of about two. As better density functionals are available for this quantity, one can concentrate on the relativistic corrections (here with respect to the LDA). One finds the following situation: While the longitudinal part agrees with the results of MBPT (at least within a factor of

Table 5. Total relativistic x-only ground state energies: Selfconsistent ROPM, RLDA and (R)GGA results for neutral atoms with closed subshells in comparison with perturbative RHF data (in *hartree* [74]).

Atom	$-E_{tot}^{L+T}$	$E_{tot}^{L+T} - E_{tot}^{L+T.ROPM}$			
	ROPM	RHF(p)	RLDA	RPW91	PW91
He	2.862	0.000	0.138	0.006	0.006
Be	14.575	-0.001	0.351	0.018	0.017
Ne	128.674	-0.002	1.080	-0.024	-0.043
Mg	199.900	-0.003	1.408	-0.001	-0.037
Ar	528.546	-0.005	2.458	0.041	-0.111
Ca	679.513	-0.006	2.818	0.026	-0.195
Zn	1793.840	-0.014	4.702	-0.263	-1.146
Kr	2787.429	-0.012	6.543	-0.022	-1.683
Sr	3176.358	-0.012	7.149	-0.010	-2.014
Pd	5041.098	-0.013	9.765	-0.069	-3.953
Cd	5589.495	-0.016	10.556	-0.035	-4.538
Xe	7441.172	-0.012	13.161	0.083	-6.706
Ba	8129.160	-0.010	14.050	0.057	-7.653
Yb	14053.748	-0.023	20.886	-0.896	-17.662
Hg	19626.702	0.005	29.159	-0.260	-27.256
Rn	23573.351	0.026	35.203	-0.012	-35.149
Ra	24996.942	0.034	37.391	-0.026	-38.271

two, but mostly better), the differences for the transverse part are much larger (up to factors of 4). The comparison should not be taken as final, as the quality of the results of MBPT is difficult to assess, but in view of the large differences, it is obvious that also the relativistic correlation-corrections need to be improved upon.

The semiempirical **relativistic GGA exchange functional** gives very reasonable results. We first consider the total energies in the x-only limit for the case of the modified PW91 functional (similar results are obtained for the other GGA x-functionals that we have investigated). For both the longitudinal as well as the full exchange the deviation from the OPM-standard is less than 0.2% (for He), for the heavier systems less than 0.01% (see Tables 4,5). If one then looks at the x-contributions (Fig.2), one finds that these quantities are also reproduced very closely (with an absolute error of less than $100mhartree$). The relativistic corrections themselves for both the longitudinal part as well as the transverse part agree very closely (which should not astonish as these quantities have been fitted).

The **relativistic GGA correlation functional** is not of the same quality (see Fig.3), still there is an order of magnitude improvement for the relativistic correlation contribution over the LDA (referred to MBPT as a standard). The fact that the situation for the correlation contribution is far from settled is

Table 6. Transverse x-only energies (E_x^T) for closed subshell atoms: ROPM results in comparison with the values obtained by insertion of ROPM densities into the relativistic LDA (RLDA) and two relativistic GGAs (RECMV92 and RB88) (all energies are in hartree, [74]).

Atom	ROPM	RLDA	RECMV92	RB88
He	0.000064	0.000159	0.000060	0.000061
Be	0.00070	0.00176	0.00071	0.00072
Ne	0.0167	0.0355	0.0166	0.0167
Mg	0.0319	0.0654	0.0319	0.0319
Ar	0.132	0.251	0.132	0.132
Ca	0.191	0.356	0.191	0.191
Zn	0.759	1.328	0.760	0.759
Kr	1.420	2.410	1.421	1.419
Sr	1.711	2.878	1.712	1.710
Pd	3.291	5.374	3.291	3.291
Cd	3.809	6.180	3.809	3.809
Xe	5.712	9.114	5.712	5.713
Ba	6.475	10.282	6.475	6.477
Yb	13.900	21.597	13.895	13.900
Hg	22.169	34.257	22.169	22.169
Rn	28.679	44.382	28.681	28.680
Ra	31.151	48.275	31.149	31.151

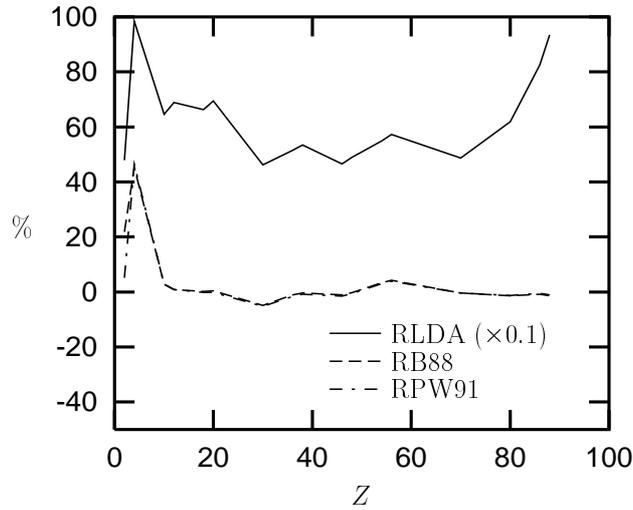


Fig. 2. Relativistic contribution ΔE_x to the x-only energy: Percentage deviation of selfconsistent RLDA and RGA results from ROPM-data for neutral atoms.

Table 7. Comparison of LDA [21], CI (estimated from nonrelativistic CI-calculations for the three innermost electrons and the experimental ionisation potentials of all other electrons [75]) and MBPT2 [57] 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

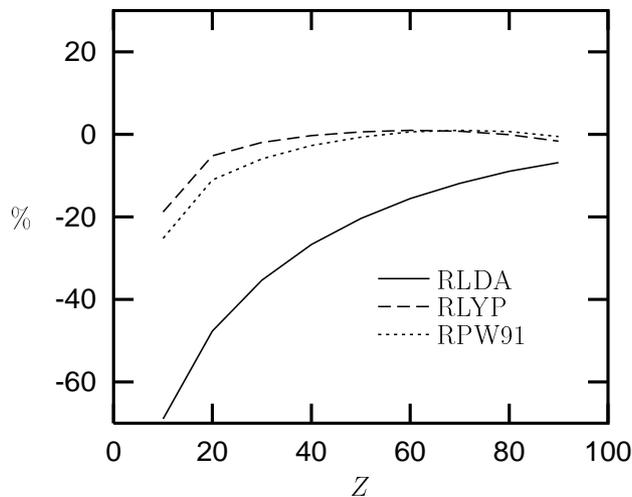


Fig. 3. Relativistic correction ΔE_c to the correlation energy: Percentage deviation of self-consistent RLDA- and RGGA-results from MBPT2-data for Ne isoelectronic series.

illustrated for the case of neutral Xe. For this case the following results are available:

$$\begin{aligned}
 \Delta E_c &= 145 \text{mhartree} && \text{RGGA [53]} \\
 &= 80 \text{mhartree} && \text{RLDA [21]} \\
 &= 146 \text{mhartree} && \text{DCB - MBPT2 [57]} \\
 &= 105 \text{mhartree} && \text{DCB - Coupled - Cluster [77]} .
 \end{aligned}$$

6 Final Remarks

Here we offer some remarks on additional points and future problems: The point that we did not discuss (although we have a large number of case studies) is the question in how far the local quantities (rather than the integrated quantities) are reasonable. This can most easily be discussed by comparison of the corresponding potentials, which show shell structure and finer effects more closely [21, 6, 52, 53].

Obviously, there is much to be done: First the calculations for atoms have to be extended to the case of nonspherical systems (with the possibility of "spin polarisation", which in the relativistic case manifests itself in the appearance of current contributions). Of greater interest is, however, the investigation of relativistic effects in more complex systems, as for instance

- i) Diatomic systems
→ changes in bond lengths, dissociation energies etc.
- ii) Solids
→ changes in band structure features (eg. Fermi surfaces) and cohesive properties
- iii) Pseudopotentials
→ as for heavy atoms even the outermost orbitals are affected by relativistic corrections, there is a modification of the pseudopotential [70]

Finally, some topics that have been addressed in the literature but have not been presented here (due to the usual lack of time), should at least be recorded.

- The discussion of RDFT has been extended to the case of strong, short range interactions on the basis of the field theoretical meson exchange model of nuclear physics, that is quantum hadrodynamics (QHD). Both ETF- [78, 79] as well as KS-applications [80, 81] have been given. In the latter instance it is of interest to note, that, due to the nature of the dominant interaction, results obtained with the x-only LDA agree quite closely with HF-results, which are available for a number of nuclei. The multiplicative character of the KS-exchange, however, allows also the consideration of superheavy nuclei [82], which, at the moment, are still not accessible via the HF-approach.
- Thermal RDFT has been discussed both on the basis of QED [83] as well as QHD [84]. Applications are restricted to thermal ETF-models [85].

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