Local and nonlocal relativistic exchange-correlation energy functionals: Comparison to relativistic optimized-potential-model results

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Relativistic corrections to the exchange-correlation energy functional of density functional theory are examined within the no-sea approximation to the full relativistic Kohn-Sham equations. We apply the relativistic optimized-potential model to spherical atoms in order to establish a comparative standard in the longitudinal exchange-only limit and use the results for an analysis of the corresponding relativistic local- and weighted-density approximations. In addition, we investigate transverse exchange and correlation contributions. A local-density approximation for the correlation energy functional is constructed from the relativistic high-density and the nonrelativistic limits and analyzed by comparison with quantum chemical data.

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I. INTRODUCTION AND SUMMARY

Density functional theory (DFT) has become a widely used tool in *ab initio* electronic structure calculations for molecules, clusters, and solids (see, e.g., [1–4]). Increased interest in DFT methods has been stimulated by the appearance of rather accurate nonlocal exchange-correlation (xc) energy functionals $E_{xc}[n]$, which have presently started to replace the former standard, the local-density approximation (LDA). For nonlocal corrections to $E_{xc}^{LDA}[n]$ a number of competing concepts have been introduced [such as the weighted density approximation [5,6] (WDA) and related schemes, the generalized gradient approximation [7,8] (GGA), or the linear response approximation [9,10]], which are currently being tested [3,11–15]. Obviously, for high-Z systems relativistic corrections should be included for the kinetic energy as well as $E_{xc}[n]$ [16–18]. However, even for systems with moderate Z relativistic contributions to E_{xc} are larger than the differences between the more refined nonlocal functionals (as, for instance, GGA's [19–22]), so that a final analysis of these functionals by comparison with experiment requires the inclusion of relativistic effects. Relativistic corrections to $E_{xc}[n]$ have been addressed in the literature [23–37], but their examination has been restricted to a limited number of systems so far. It is the purpose of this contribution to provide an overview of the accuracy that can be obtained with currently available relativistic $E_{xc}[n]$ and to establish a definitive comparative standard, at least for longitudinal exchange-only potentials and energies.

Relativistic DFT (RDFT) [23,25,27,36] constitutes a rather general approach to the ground state properties of atomic, molecular, and condensed matter systems including not only magnetic but also quantum electrodynamical effects. On the most general level, however, the RDFT formalism is very complicated and computationally involved, mostly due to the self-consistent inclusion of radiative corrections [36]. On the other hand, if one aims at electronic

structure calculations for atoms, molecules, and solids, radiative effects can either be neglected completely (no-sea approximation) or need not be taken into account self-consistently: If required at all, a perturbative treatment should prove to be sufficient, except in special circumstances. Excluding in addition the presence of external magnetic fields, one ends up with a calculational scheme which differs from nonrelativistic DFT only by the Dirac form of the relativistic Kohn-Sham (RKS) equations and relativistic corrections to the functional dependence of $E_{xc}[n]$ on n. Finally, in most situations also photon retardation effects, i.e., the contribution of transverse photons, only play a minor role. This suggests including only the longitudinal electron-electron (Coulomb) interaction self-consistently, while adding all transverse (Breit) contributions in a perturbative manner [38]. (This approximation is by no means essential for RDFT applications.) The resulting scheme should provide a reasonable starting point for electronic structure calculations and is particularly suited for an examination of approximation schemes for $E_{xc}[n]$. We note, however, that due to the intrinsic coupling of orbital angular momentum and electron spin no relativistic analogue of spin-density functional theory is currently available. The RDFT formalism is briefly reviewed in Sec. II in order to establish the longitudinal no-sea RKS equations, initially introduced in the context of the relativistic Slater approach [39].

For an analysis of approximations for $E_{xc}[n]$ the availability of an exact reference standard is of importance. In the nonrelativistic case it turned out to be useful to compare the xc potentials $v_{xc}(r)$ in a given approximation with the corresponding exact results [22,40–43] rather than the total xc energies E_{xc}: Local errors which are clearly recognizable in $v_{xc}(r)$ can cancel in E_{xc}, so that the potentials are more suitable to reveal the physical content and the accuracy of the approximation. Unfortunately, the evaluation of exact local xc potentials for larger atoms represents a formidable task even in the nonrelativistic limit. Consequently, results for relativistic v_{xc} are not available at present. On the other hand, the exact longitudinal exchange-only (x-only) potential v_x^L can be evaluated rather directly even in the relativistic case, so that this limit can be used for a detailed study of

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local or improved approximations. Thus the first aim of this paper is to provide a rigorous comparative standard for both atomic exchange energies and potentials, which, due to the multiplicative nature of the corresponding exchange potential, is based on the relativistic extension of the optimized-potential-model [44–48] (OPM) rather than on the Hartree-Fock (HF) approximation. The relativistic OPM (ROPM) [49] approach is summarized in Sec. III. Moreover, it is shown that ROPM results for ground state and exchange energies of atoms (with closed subshells, i.e., atoms with spherical symmetry in the x-only limit) are very close to the corresponding relativistic HF (RHF) values.

The ROPM results of Sec. III then allow us to examine the LDA [50–52,25,27] for the relativistic $E_x[n]$ in some detail (in Sec. IV A). Unfortunately, it turns out that the relativistic LDA (RLDA) underestimates the relativistic contribution to the longitudinal exchange energy E_x^L by 20–50 % (with a tendency of becoming more accurate with increasing Z), while it overestimates the transverse component of the exchange energy, E_x^T, by about 50% (as already noted by MacDonald and Vosko [27] and Ramana et al. [32]). The failure of the RLDA to represent the relativistic components of $E_x^L[n]$ is even more obvious from a comparison of the x-only RLDA potential to the exact v_x^{ROPM}: The RLDA potential shows substantial deviations from v_x^{ROPM} in the small-r region which are also reflected by the corresponding single-particle energies. As one might have expected, the relativistic corrections to E_x^L and v_x^L are dominated by the self-interaction of the $1S_{1/2}$ electrons. This can be gleaned from the similarity of the relativistic corrections to neutral atoms and the corresponding ions with only two bound electrons. It is therefore not surprising that the RLDA shows significant errors, as even in the nonrelativistic case an accurate treatment of self-interaction effects is known to require highly nonlocal exchange functionals.

This then suggests the consideration of a nonlocal approximation which explicitly takes into account electron self-interaction effects. One of the most widely used schemes of this type is the WDA, its crucial ingredient being a density functional representation of the x-only pair correlation function g_x. While for the nonrelativistic g_x rather refined approximations have been suggested in the literature [53–56], their relativistic generalization is not immediately obvious. We thus use the only relativistic g_x available at present, the pair correlation function of the relativistic homogeneous electron gas (RHEG), g_x^{RHEG} [24,27], for a first study of the properties of the relativistic WDA (RWDA). A simple and accurate fit to g_x^{RHEG} which simplifies the actual RWDA calculations is provided in the Appendix. The relativistic corrections for E_x^L and v_x^L obtained from the RWDA are closer to the ROPM results than those from the RLDA.

Finally, in Sec. V we examine the RLDA for the relativistic correlation energy functional $E_c[n]$. As the correlation energy of the RHEG has only been calculated within the ring approximation (RPA) [31,57], which constitutes the most relevant contribution only in the high-density regime, the difference between the relativistic RPA and its nonrelativistic limit is combined with the full nonrelativistic LDA for $E_c[n]$ in order to establish a more complete RLDA. A comparison of atomic E_c's from the RLDA with quantum chemi-

cal results for the correlation energy demonstrates that the relativistic corrections to E_c are much smaller than those to E_x and that the RLDA is only correct within a factor of 2, even for high-Z atoms. In particular, the relativistic correction to the longitudinal correlation energy is overestimated (for neutral high-Z atoms by roughly 30%), while the transverse correlation energy is by far underestimated.

One is thus led to the conclusion that nonlocal corrections for both $E_x[n]$ and $E_c[n]$ are even more important in the relativistic context than they are in the nonrelativistic situation. Consequently, intrinsically nonlocal concepts like the WDA seem suitable to account for relativistic corrections to $E_{xc}[n]$. It remains to be investigated whether semilocal approaches like GGA's allow a sufficiently accurate treatment of these corrections.

II. THEORETICAL BACKGROUND

A relativistic extension of the Hohenberg-Kohn (HK) theorem [9] has first been formulated by Rajagopal and Callaway [23]. The corresponding relativistic Kohn-Sham equations have been introduced by Rajagopal [25] and by MacDonald and Vosko [27]. A more detailed discussion of the quantum electrodynamical basis of RDFT, addressing in particular questions of renormalization, has been given in a recent review [36] to which we also refer the reader for an overview of RDFT. Here we only summarize its central features: Any (nondegenerate) ground state $|\Phi_0\rangle$ corresponding to some given external four potential $v_{ext}^\mu(r)$ is, up to gauge transformations, uniquely determined by the renormalized ground state four current $j_R^\mu(r)$ of the system, i.e., the ground state is a unique (and universal) functional of the four current, $|\Phi_0[j_R^\mu]\rangle$. As a consequence the ground state energy E_0 can also be viewed as a functional of the complete $j_R^\mu(r)$, $E_0[j_R^\mu]$. Minimization of $E_0[j_R^\mu]$ then leads to the exact ground state four current and energy, including all vacuum effects inherent in the underlying quantum field theory, i.e., quantum electrodynamics (QED). In order to set up the RKS equations one introduces auxiliary single-particle four spinors φ_k to represent $j_R^\mu(r)$ as

$$j_R^\mu(r) = j_V^\mu(r) + j_D^\mu(r), \qquad (2.1)$$

$$j_V^\mu(r) = \frac{1}{2} \left\{ \sum_{\epsilon_k \leq -mc^2} \bar{\varphi}_k(r) \gamma^\mu \varphi_k(r) \right.$$

$$\left. - \sum_{-mc^2 < \epsilon_k} \bar{\varphi}_k(r) \gamma^\mu \varphi_k(r) \right\}, \qquad (2.2)$$

$$j_D^\mu(r) = \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \bar{\varphi}_k(r) \gamma^\mu \varphi_k(r), \qquad (2.3)$$

where the vacuum (V) and the occupied orbital (D) contributions have already been separated [renormalization is implicitly understood in the case of $j_V^\mu(r)$]. One can then decompose the total ground state energy functional $E_0[j^\nu]$ into the kinetic energy functional of noninteracting electrons $T_s[j^\nu]$ (we use $\hbar = 1$ throughout this paper),

$$T_s^R = T_s^V + T_s^D, \qquad (2.4)$$

$$T_s^D = \int d^3r \sum_{-mc^2 < \epsilon_k \leqslant \epsilon_F} \bar{\varphi}_k(r)[-ic\,\boldsymbol{\gamma}\cdot\nabla + mc^2]\varphi_k(r),$$

$$(2.5)$$

where T_s^V has a similar structure as j_V^μ and also requires renormalization [36], the external potential energy

$$E_{\text{ext}} = \int d^3r \; j_\mu(r)v_{\text{ext}}^\mu(r),$$

$$(2.6)$$

the "covariant" Hartree energy,

$$E_H = -i\,\frac{e^2}{2}\int d^3x \int d^4y\, j^\mu(x)D_{\mu\nu}^0(x-y)j^\nu(y), \quad (2.7)$$

where $D_{\mu\nu}^0(x-y)$ represents the free photon propagator,

$$D_{\mu\nu}^0(x-y) = -ig_{\mu\nu}\int \frac{d^4k}{(2\pi)^4}\frac{4\pi e^{-ik(x-y)}}{(k^2+i\epsilon)} \quad (2.8)$$

(Feynman gauge), and the xc energy functional $E_{xc}[j^\nu]$,

$$E_0[j^\nu] = T_s[j^\nu] + E_{\text{ext}}[j^\nu] + E_H[j^\nu] + E_{xc}[j^\nu], \quad (2.9)$$

and recast the energy minimization in the form of Dirac-type RKS equations [25,27,36,37].

However, these RKS equations are rather involved due to the four-component structure of both the Hartree and the xc potential and, even more importantly, due to the fact that the vacuum polarization current $j_V^\mu(r)$ enters the self-consistency procedure, requiring summation over all continuum states. Thus, while RDFT provides a rather general and extremely powerful approach to relativistic bound state problems in principle, some physically motivated approximations seem unavoidable in order to make RDFT a workable scheme in practice. Aiming at electronic structure calculations for molecules and solids the following simplifications should be appropriate, in particular, in view of the limitations of present xc energy functionals, even on the nonrelativistic level.

(i) First of all, a more modest approach only aiming at relativistic but neglecting radiative corrections (often called the no-sea approximation) suggests itself. This amounts to dropping $j_V^\mu(r)$ from the four current, Eq. (2.1), and to ignoring all vacuum corrections in both the kinetic as well as the xc energy functional. In any case an *a posteriori* perturbative evaluation of radiative corrections should be sufficient for most problems of interest and, in fact, represents the standard treatment (compare, e.g., [59]).

(ii) While according to the relativistic HK theorem in general the complete $j^\mu(r)$ is required to determine $|\Phi_0\rangle$, knowledge of its zeroth component, $j^0(r) = n(r)$, is sufficient if the spatial components of the external potential vanish, $v_{\text{ext}} = 0$ (which does not only exclude the presence of external magnetic fields but also implies a partial fixing of gauge). As this is the situation most commonly met in electronic structure calculations, we will restrict the present discussion to this "electrostatic" limit. Note, however, that this does not imply that the spatial components of the current vanish in general, but rather that $j(r) = \langle\Phi_0[n]|\hat{j}(r)|\Phi_0[n]\rangle$ has to be interpreted as a functional of $n(r)$.

(iii) Finally, one can split $E_H[n]$ as well as $E_{xc}[n]$ into their longitudinal (Coulomb) and transverse components,

$$E_H[n] = E_H^L[n] + E_H^T[n], \quad (2.10)$$

$$E_{xc}[n] = E_{xc}^L[n] + E_{xc}^T[n]. \quad (2.11)$$

The definition of the individual components relies on the corresponding decomposition of the photon propagator $D_{\mu\nu}^0(x-y)$ into the nonretarded Coulomb (longitudinal) interaction and the transverse contribution [59],

$$D_{\mu\nu}^0(x-y) = ig_{0\mu}g_{0\nu}\frac{\delta(x^0-y^0)}{|\mathbf{x}-\mathbf{y}|} + D_{\mu\nu}^{0,T}(x-y).$$

$$(2.12)$$

The longitudinal components $E_H^L[n]$ and $E_{xc}^L[n]$ are obtained from $E_H[n]$ and $E_{xc}[n]$ by neglecting $D_{\mu\nu}^{0,T}(x-y)$ completely (while this decomposition is immediately clear for $E_H[n]$, explicit examples for $E_{xc}[n]$ will be given in Secs. IV and V). Following the standard treatment within the relativistic HF approach [38,58], it seems legitimate in most situations to add $E_H^T[n]$ and $E_{xc}^T[n]$ as perturbative corrections, i.e., to neglect the corresponding potentials $v_H^T[n]$ and $v_{xc}^T[n]$ in the self-consistency loop. While, in contrast to the previous two simplifications, this approximation is not required for an efficient application of the RKS equations, it allows a more direct comparison of the resulting RDFT data to most conventional many-body results. Moreover, for all the atomic systems considered in this work the self-consistent inclusion of $E_H^T[n]$ and $E_{xc}^T[n]$ leads to results which are only marginally different from the perturbative ones.

The resulting longitudinal no-sea RKS equations then read

$$\{-ic\,\boldsymbol{\alpha}\cdot\nabla + \beta mc^2 + v^{\text{RKS}}(r)\}\varphi_k(r) = \epsilon_k\varphi_k(r), \quad (2.13)$$

where

$$v^{\text{RKS}}(r) = v_{\text{ext}}(r) + v_H^L(r) + v_{xc}^L([n];r), \quad (2.14)$$

$$v_H^L(r) = e^2\int d^3r'\,\frac{n(r')}{|r-r'|}, \quad (2.15)$$

$$v_{xc}^L([n];r) = \frac{\delta E_{xc}^L[n]}{\delta n(r)}, \quad (2.16)$$

$$n(r) = \sum_{-mc^2 < \epsilon_k \leqslant \epsilon_F} \varphi_k^\dagger(r)\varphi_k(r). \quad (2.17)$$

The longitudinal ground state energy of the system is obtained from

$$E_{\text{tot}}^L = T_s^D + E_{\text{ext}} + E_H^L + E_{xc}^L, \quad (2.18)$$

while the transverse energy components are evaluated perturbatively using the result of (2.13),

$$E_{\text{tot}} = E_{\text{tot}}^L + E_H^T[n] + E_{xc}^T[n]. \quad (2.19)$$

If desired, radiative corrections can be added at this point (in this contribution, however, vacuum effects will be completely neglected).

It should be emphasized that the calculational procedure suggested here for the application of RDFT closely follows the standard relativistic many-body approach: It essentially represents the RDFT equivalent of the so-called no-pair Dirac-Coulomb Hamiltonian [18] (self-consistent treatment of $E_H^T[n]+E_{xc}^T[n]$ would lead to the RDFT version of the no-pair Dirac-Coulomb-Breit Hamiltonian, neglecting the small differences between the full transverse interaction and its Breit limit as well as between the no-pair and the no-sea approximation). In Secs. IV and V the approach characterized by Eqs. (2.13)–(2.19) is used to analyze various approximations for $E_{xc}[n]$ for spherical atoms. We remark that E_H^T vanishes for these systems,

$$E_H^T = -\frac{e^2}{2} \int d^3r \int d^3r' \frac{\mathbf{j}(\mathbf{r}) \cdot \mathbf{j}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = 0, \qquad (2.20)$$

as $\mathbf{j}(\mathbf{r}) = \mathbf{0}$.

III. RELATIVISTIC OPTIMIZED-POTENTIAL MODEL

In close analogy to the nonrelativistic case, the exchange-only limit of the xc energy functional is defined by insertion of the RKS four spinors φ_k into the relativistic Fock term. For the exact longitudinal exchange energy functional [60] one thus obtains

$$E_x^L[n] = -\frac{e^2}{2} \int d^3r \int d^3r'$$

$$\times \sum_{-mc^2 < \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\varphi_{a,k}^{\dagger}(\mathbf{r})\varphi_{b,l}^{\dagger}(\mathbf{r}')\varphi_{a,l}(\mathbf{r})\varphi_{b,k}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$$

$$(3.1)$$

where the φ_k have to be interpreted as functionals of the density and summation over the spinor indices $a,b=1,\ldots,4$ is implicitly understood. The crucial feature of this $E_x^L[n]$ is its linear dependence on the electron-electron coupling constant e^2, which relies on the fact that the functional dependence of the φ_k on n is independent of e^2 as the φ_k experience a local (in the sense of multiplicative) one-body potential [46–48]. While the exact density dependence of $E_x^L[n]$ is not known, the corresponding x-only potential $v_x^L(\mathbf{r})$ can nevertheless be obtained by solution of the ROPM equations [45], utilizing the fact that the one-body potential minimizing the x-only ground state energy $T_s^D + E_{\text{ext}} + E_H^L + E_x^L$ is unique [46–48]. The ROPM equations require the simultaneous self-consistent solution of the RKS equations (2.13) in the x-only limit, i.e., with the local RKS potential

$$v^{\text{ROPM}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_H^L(\mathbf{r}) + v_x^L(\mathbf{r}), \qquad (3.2)$$

and the ROPM integral equation [45],

$$\int d^3r' \, K(\mathbf{r},\mathbf{r}')v_x^L(\mathbf{r}') = Q(\mathbf{r}), \qquad (3.3)$$

where

$$K(\mathbf{r},\mathbf{r}') = \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \varphi_k^{\dagger}(\mathbf{r})G_k(\mathbf{r},\mathbf{r}')\varphi_k(\mathbf{r}') \qquad (3.4)$$

and

$$Q(\mathbf{r}) = -e^2 \sum_{-mc^2 < \epsilon_k, \epsilon_l \leq \epsilon_F} \int d^3r' \int d^3r'',$$

$$\times \varphi_k^{\dagger}(\mathbf{r})G_k(\mathbf{r},\mathbf{r}')\frac{\varphi_l(\mathbf{r}')\varphi_l^{\dagger}(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|}\varphi_k(\mathbf{r}''). \qquad (3.5)$$

Here $G_k(\mathbf{r},\mathbf{r}')$ represents the Green's function

TABLE I. Longitudinal x-only ground state energies ($-E_{\text{tot}}^L$) for closed subshell atoms from nonrelativistic OPM (NROPM), relativistic OPM (ROPM), relativistic HF (RHF), RNRLDA, RLDA, and RWDA calculations [61] (all energies are in hartrees).

Atom	NROPM	ROPM	RHF	RNRLDA	RLDA	RWDA
He	2.862	2.862	2.862	2.724	2.724	2.862
Be	14.572	14.575	14.576	14.226	14.226	14.609
Ne	128.545	128.690	128.692	127.635	127.628	129.417
Mg	199.611	199.932	199.935	198.569	198.556	200.963
Ar	526.812	528.678	528.684	526.387	526.337	530.747
Ca	676.751	679.704	679.710	677.118	677.047	682.204
Zn	1777.828	1794.598	1794.613	1790.721	1790.458	1799.949
Kr	2752.028	2788.848	2788.861	2783.758	2783.282	2795.778
Sr	3131.514	3178.067	3178.080	3172.638	3172.071	3185.631
Pd	4937.858	5044.384	5044.400	5037.733	5036.677	5054.707
Cd	5465.056	5593.299	5593.319	5586.299	5585.086	5604.337
Xe	7232.018	7446.876	7446.895	7438.858	7437.076	7460.124
Ba	7883.404	8135.625	8135.644	8127.344	8125.336	8149.714
Yb	13391.070	14067.621	14067.669	14058.528	14054.349	14089.603
Hg	18408.313	19648.826	19648.865	19638.195	19631.622	19675.706
Rn	21865.826	23601.969	23602.005	23590.763	23582.293	23632.105
Ra	23093.258	25028.027	25028.061	25016.763	25007.568	25059.377
No	32787.471	36740.625	36740.682	36730.804	36714.839	36782.219

$$G_k(r,r') = \sum_{-mc^2 < \epsilon_l < mc^2,\ l \neq k} \frac{\varphi_l(r)\varphi_l^\dagger(r')}{\epsilon_l - \epsilon_k}, \qquad (3.6)$$

which satisfies

$$[-ic\boldsymbol{\alpha}\cdot\nabla + \beta mc^2 + v^{\text{ROPM}}(r) - \epsilon_k]G_k(r,r')$$

$$= \delta^{(3)}(r-r') - \varphi_k(r)\varphi_k^\dagger(r'). \qquad (3.7)$$

For spherical atoms the ROPM integral equation can, as in the nonrelativistic case, be solved on a discrete mesh (here 800 mesh points have been used). Note that Eq. (3.3) determines v_x^L only up to an additive constant, which is specified by requiring the exact asymptotic form [45] of the ROPM exchange potential, $v_x^L(r\to\infty)\to -e^2/r$.

Some ROPM results for spherical (closed subshell) atoms are compared to RHF- [58] and nonrelativistic OPM data [41] in Tables I–III [61]. First of all, Table I lists the longitudinal ground state energies E_{tot}^L, demonstrating on the one hand the drastic relativistic effects for high-Z atoms and on the other hand the similarity of ROPM and RHF results. In fact, the differences between ROPM and RHF total energies are smaller than 60 mhartree, with the ROPM energies always being somewhat higher (consistent with the reduced variational freedom of the ROPM orbitals) — apart from He, where both approaches coincide. An analogous agreement between ROPM and RHF results is found for the longitudinal exchange energies E_x^L given in Table II. Here the maximum difference amounts to 106 mhartree (obtained for No). On the other hand, the relativistic contributions to E_x^L,

$$\Delta E_x = E_x^L[n^R] - E_x^{NR}[n^{NR}], \qquad (3.8)$$

i.e., the differences between the ROPM and the nonrelativistic OPM values, are quite remarkable. For instance, for Hg

one obtains 20 hartree (see Table II), which represents 5.8% of E_x^L, very similar to the 6.8% relativistic correction found for E_{tot}^L.

Clearly, relativistic effects are most important for the innermost orbitals. This is obvious from Table III, showing the single-particle spectrum of Hg. Note, however, that the $2P_{1/2}$ eigenvalue is also modified by 17% and even the outermost $6S_{1/2}$ eigenvalue experiences a 26% shift (reflecting the "gold maximum"). Table III also demonstrates that, apart from the physically relevant highest occupied eigenvalue and in spite of the very similar ground state energies, ROPM and RHF single-particle energies differ substantially (compare [40]), in consistency with their auxiliary character.

IV. RELATIVISTIC EXCHANGE-ONLY ENERGY FUNCTIONALS

A. Local-density approximation

Among the nonrelativistic xc energy functionals the LDA represents the most widely used approximation and thus also serves as a starting point in the relativistic case. In the LDA the density dependence of the xc energy density e_{xc} of the HEG is used with the substitution of the constant density n_0 by the local density $n(r)$ of the inhomogeneous system in question. The x-only energy of the RHEG has been evaluated a number of times [50–52,25,27]. For the longitudinal component one finds [52,27]

$$E_x^{L,\text{RLDA}}[n] = \int d^3r\ e_x^{\text{NRLDA}}(n)\Phi^L(\beta), \qquad (4.1)$$

$$e_x^{\text{NRLDA}}(n) = -\frac{3(3\pi^2)^{\frac{1}{3}}e^2}{4\pi}n^{\frac{4}{3}}, \qquad (4.2)$$

TABLE II. Longitudinal (Coulomb) exchange energies $(-E_x^L)$ for closed shell atoms from NROPM, ROPM, RHF, RNRLDA, RLDA, and RWDA calculations [61] (all energies are in hartrees).

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

TABLE III. Single-particle energies $(-\epsilon_{nlj})$ for Hg from nonrelativistic (NROPM) and relativistic (ROPM) OPM calculations as well as relativistic HF (RHF) results in comparison to the eigenvalues obtained by solution of (2.13) using various x-only energy functionals: RNRLDA: nonrelativistic LDA, Eq. (4.9); RLDA: relativistic LDA, Eq. (4.1); RWDA: relativistic WDA, Eq. (4.21). Also listed are the eigenvalues from the complete longitudinal RLDA xc energy functional [RLDA(x+c)], Eqs. (4.1) and (5.5) [61] (all energies are in hartrees).

Level	NROPM	ROPM	RHF	RNRLDA	RLDA	RWDA	RLDA(x+c)
$1S_{1/2}$	2756.925	3047.430	3074.228	3047.517	3044.410	3051.995	3044.573
$2S_{1/2}$	461.647	540.056	550.251	539.713	539.250	540.530	539.342
$2P_{1/2}$	444.015	518.061	526.855	518.164	517.746	519.244	517.840
$2P_{3/2}$	444.015	446.682	455.157	446.671	446.399	447.469	446.488
$3S_{1/2}$	108.762	128.272	133.113	128.001	127.905	128.292	127.976
$3P_{1/2}$	100.430	118.350	122.639	118.228	118.148	118.592	118.220
$3P_{3/2}$	100.430	102.537	106.545	102.397	102.346	102.691	102.416
$3D_{3/2}$	84.914	86.201	89.437	86.085	86.060	86.364	86.131
$3D_{5/2}$	84.914	82.807	86.020	82.690	82.668	82.959	82.739
$4S_{1/2}$	23.522	28.427	30.648	28.067	28.046	28.200	28.109
$4P_{1/2}$	19.895	24.161	26.124	23.871	23.854	24.023	23.917
$4P_{3/2}$	19.895	20.363	22.189	20.039	20.030	20.167	20.092
$4D_{3/2}$	13.222	13.411	14.797	13.148	13.146	13.271	13.207
$4D_{5/2}$	13.222	12.700	14.053	12.434	12.432	12.553	12.493
$4F_{5/2}$	4.250	3.756	4.473	3.556	3.559	3.665	3.618
$4F_{7/2}$	4.250	3.602	4.312	3.402	3.404	3.509	3.464
$5S_{1/2}$	3.501	4.403	5.103	4.290	4.286	4.349	4.339
$5P_{1/2}$	2.344	3.012	3.538	2.898	2.896	2.955	2.949
$5P_{3/2}$	2.344	2.363	2.842	2.219	2.218	2.265	2.271
$5D_{3/2}$	0.538	0.505	0.650	0.363	0.363	0.397	0.413
$5D_{5/2}$	0.538	0.439	0.575	0.296	0.296	0.328	0.345
$6S_{1/2}$	0.262	0.329	0.328	0.222	0.222	0.254	0.262

$$\Phi^L(\beta) = \frac{5}{6} + \frac{1}{3\beta^2} + \frac{2\eta}{3\beta}\,\text{arcsinh}(\beta) - \frac{2\eta^4}{3\beta^4}\ln(\eta)$$

$$- \frac{1}{2}\left(\frac{\eta}{\beta} - \frac{\text{arcsinh}(\beta)}{\beta^2}\right)^2, \qquad (4.3)$$

$$\beta = \frac{(3\pi^2 n)^{\frac{1}{3}}}{mc}, \qquad (4.4)$$

$$\eta = (1+\beta^2)^{\frac{1}{2}}, \qquad (4.5)$$

while the corresponding transverse component is given by [52,27]

$$E_x^{T,\text{RLDA}}[n] = \int d^3r\, e_x^{\text{NRLDA}}(n)\Phi^T(\beta), \qquad (4.6)$$

$$\Phi^T(\beta) = \frac{1}{6} - \frac{1}{3\beta^2} - \frac{2\eta}{3\beta}\,\text{arcsinh}(\beta) + \frac{2\eta^4}{3\beta^4}\,\ln(\eta)$$

$$- \left(\frac{\eta}{\beta} - \frac{\text{arsinh}(\beta)}{\beta^2}\right)^2. \qquad (4.7)$$

Plots of $\Phi^L(\beta)$ and $\Phi^T(\beta)$ (and their various components, such as the Breit term) can be found in [27,36]. As in the nonrelativistic case, Eq. (4.1) represents the homogeneous limit of the exact $E_x^L[n]$, Eq. (3.1).

Before proceeding to a detailed analysis of the RLDA a few remarks concerning conceptual questions seem in order.

(i) First of all, the effect of using finite versus point nuclei has to be discussed [61]. While, as is well known, the ground state energy and the innermost single-particle energies for finite and point nuclei differ substantially, Table IV demonstrates that the exchange energy is only marginally affected: For Hg, which we use as a prototype of all high-Z atoms, the difference of 58 mhartree between the longitudinal RHF x-only energies for point and finite nuclei is negligible compared to the difference of 17.6 hartree between the RLDA (347.659 hartree) and the RHF values. This is corroborated from a local perspective in Figs. 1 and 2, where the radial density $4\pi r^2 n(r)$ and the relativistic correction to the x-only potential,

$$\Delta v_x(r) = \frac{v_x^L([n^R];r) - v_x^{\text{NR}}([n^{\text{NR}}];r)}{v_x^{\text{NROPM}}([n^{\text{NROPM}}];r)}, \qquad (4.8)$$

TABLE IV. Relativistic HF results for Hg: Point versus finite nucleus [61] (for Hg the nuclear radius is $R = 0.000\ 133$ a.u.) (all energies are in hartrees).

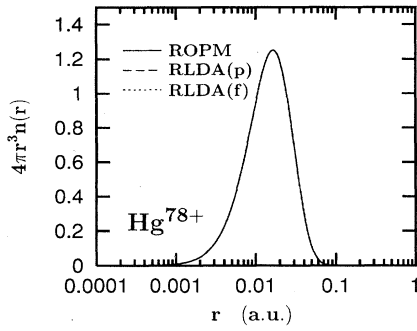| Nucleus	$-E_{\text{tot}}^L$	$-\epsilon_{1S1/2}$	$-E_x^L$	E_x^T
Point	19 653.649	3076.157	365.335	22.184
Finite	19 648.864	3074.228	365.277	22.166

FIG. 1. Radial densities $4\pi r^2 n(r)$ obtained for Hg^{78+} by self-consistent ROPM (using a finite nucleus) and RLDA calculations using both a point (p) and a finite (f) nucleus [61].

i.e., the percentage deviation of the self-consistent relativistic potential $v_x^L([n^R];r)$ from the corresponding self-consistent nonrelativistic potential $v_x^{NR}([n^{NR}];r)$, are shown for Hg^{78+}. Note that for a given (approximate) $E_x^L[n]$ the self-consistent relativistic potential $v_x^L([n^R];r)$ is calculated by insertion of the self-consistent relativistic density $n^R(r)$ into the functional derivative (2.16) for that $E_x^L[n]$ which has been used to determine $n^R(r)$. In particular, the ROPM x-only potential can formally be understood as being obtained by insertion of the exact density $n^{ROPM}(r)$ into the exact $v_x^L([n],r) = v_x^{ROPM}([n];r)$. The same holds for the nonrelativistic OPM (NROPM) potential $v_x^{NROPM}([n^{NROPM}];r)$, which is used for normalization in (4.8). As a consequence $\Delta v_x(r)$ is a direct measure of the corresponding relativistic correction to $n^{NR}(r)$. In fact, the radial densities obtained for the point and the finite nucleus [using the RLDA, Eq. (4.1), in both cases] are indistinguishable. Even for rather small r (apart from the immediate vicinity and the interior of the nucleus) the density and thus $v_x^L([n^R];r)$ do not depend sensitively on the form of the nucleus, a feature that is exhibited more clearly by $\Delta v_x(r)$ (Fig. 2). In particular, the divergence of the RLDA x-only potential at the origin resulting from the divergence of $n(r)$
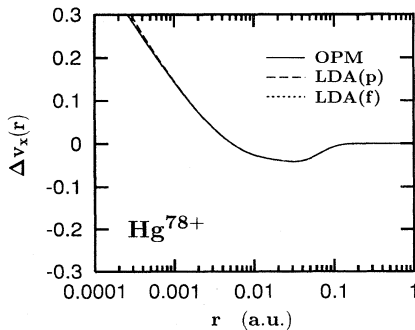

FIG. 2. Relativistic correction to the longitudinal x-only potential $\Delta v_x(r)$, Eq. (4.8), for Hg^{78+} obtained by insertion of self-consistent OPM (using a point nucleus) and LDA densities [using both a point (p) and a finite (f) nucleus [61]] into the $v_x^L[n]$ resulting from (4.1) [the nonrelativistic LDA x-only potential has always been used for $v_x^{NR}(r)$].

TABLE V. Relativistic contribution to the longitudinal exchange energy ($-\Delta E_x$) from self-consistent OPM, RNRLDA, LDA, WDA and calculations [61] (all energies are in hartrees).

Atom	OPM	RNRLDA	LDA	WDA
He	0.000	0.000	0.000	0.000
Be	0.001	0.001	0.000	0.001
Ne	0.015	0.015	0.007	0.015
Mg	0.029	0.029	0.015	0.029
Ar	0.118	0.122	0.069	0.122
Ca	0.172	0.179	0.104	0.178
Zn	0.627	0.675	0.402	0.662
Kr	1.215	1.306	0.814	1.278
Sr	1.478	1.590	1.005	1.555
Pd	2.785	3.042	1.958	2.957
Cd	3.264	3.566	2.322	3.461
Xe	5.021	5.481	3.657	5.312
Ba	5.739	6.269	4.215	6.073
Yb	12.043	13.450	9.194	12.920
Hg	19.963	22.421	15.734	21.518
Rn	26.637	29.918	21.307	28.696
Ra	29.241	32.859	23.513	31.503
No	52.403	59.886	43.683	57.074

for point nuclei does not show up in the relevant r regime (for high density $v_x^{L,RLDA}[n] \sim n^{1/3}$ [27]). Nevertheless, the subsequent analysis of $E_x[n]$ (and also $E_c[n]$) is based on finite nuclei [61,62].

(ii) Furthermore, as $v_x^L(r)$ only represents a small fraction of the total potential experienced by the $1S_{1/2}$ electrons the $1S_{1/2}$ density distribution is almost independent of the specific functional form of $v_x^L[n]$ used in the RKS equations. This is demonstrated in Figs. 1 and 2 where also the radial ROPM density and the $\Delta v_x(r)$ obtained by insertion of the ROPM density into the $v_x^L[n]$ resulting from (4.1) (and n^{NROPM} into $v_x^{NRLDA}([n],r)$) are given: $n^{ROPM}(r)$ is very close to the RLDA density, although one finds a non-negligible difference between the ROPM and RLDA $1S_{1/2}$ single-particle energies (see Table III) reflecting the different asymptotic behavior of the densities. One thus concludes that $n(r)$ is not the most suitable quantity on which a comparison of different approximations for $E_x^L[n]$ could be based. A direct look at the corresponding self-consistent $v_x^L(r)$ allows us to distinguish various approximations to $v_x^L[n]$ much more clearly.

(iii) As a consequence the x-only energies obtained by insertion of different self-consistent relativistic densities $n^R(r)$ into some approximate $E_x^L[n]$ are rather similar [27,32]: Using, e.g., the ROPM density for Hg in Eq. (4.1) leads to -347.928 hartree compared to -347.612 hartree found by insertion of the self-consistent RLDA density.

With these considerations in mind we now proceed to an analyis of the x-only RLDA, Eqs. (4.1) and (4.6). In spite of its early appearance in the literature the x-only RLDA has only rarely been used in actual applications [28,29,32]. This may be attributed to the fact [32] that nonlocal contributions play an important role in the relativistic corrections to the x-only energy. This is confirmed by Table V, in which the ΔE_x from the RLDA, Eq. (4.1), is compared to the exact

ROPM values and the ΔE_x found by using the nonrelativistic x-only LDA functional,

$$E_x^{\text{NRLDA}}[n] = \int d^3r \; e_x^{\text{NRLDA}}(n), \qquad (4.9)$$

in the RKS equations (this computational scheme, usually referred to as the Dirac-Fock-Slater approach with $\alpha = 2/3$, is abbreviated by RNRLDA here). While for larger Z the RNRLDA overestimates the ROPM results by about 10%, the RLDA underestimates them drastically, in particular for low and intermediate Z.

In order to analyze the origin of this failure of the RLDA it is useful to separate the two effects leading to the relativistic correction in x-only energies,

$$\Delta E_x = \Delta E_x(\text{dens}) + \Delta E_x(\text{fctl}), \qquad (4.10)$$

$$\Delta E_x(\text{dens}) = E_x^{\text{NR}}[n^R] - E_x^{\text{NR}}[n^{\text{NR}}], \qquad (4.11)$$

$$\Delta E_x(\text{fctl}) = E_x^L[n^R] - E_x^{\text{NR}}[n^R], \qquad (4.12)$$

i.e., the correction $E_x^{\text{NR}}[n^R] - E_x^{\text{NR}}[n^{\text{NR}}]$ resulting from the difference between the self-consistent relativistic density n^R and the self-consistent nonrelativistic density n^{NR} and the contribution $E_x^L[n^R] - E_x^{\text{NR}}[n^R]$ arising from the relativistic modification of the functional dependence of the x-only functional on n. Using, e.g., the RLDA one finds for Hg $\Delta E_x(\text{dens}) = -22.303$ hartree and $\Delta E_x(\text{fctl}) = 6.569$ hartree. Thus the dominating density contribution increases the x-only energy, while the functional correction leads to a reduction (as is immediately obvious from the form of Φ^L). Note that the $\Delta E_x(\text{dens})$ contribution is dominated by the relativistic corrections to the kinetic energy and thus is rather insensitive to the precise form of $E_x^L[n]$. Consequently the $\Delta E_x(\text{dens})$ from the LDA is almost identical to the complete ΔE_x from the RNRLDA (-22.421 hartree for Hg). $\Delta E_x(\text{fctl})$, on the other hand, is exclusively determined by the properties of $E_x^L[n]$, making it a particularly interesting analytic tool.

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

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

is identical to the exact $E_x^{\text{NR}}[n]$. The OPM values of $\Delta E_x(\text{dens}) = -7.963$ hartree and $\Delta E_x(\text{fctl}) = 0$ for Hg^{78+} can thus be compared to the corresponding LDA results, $\Delta E_x^{\text{LDA}}(\text{dens}) = -7.198$ hartree and $\Delta E_x^{\text{LDA}}(\text{fctl}) = 3.157$ hartree. The error of 765 mhartree for $\Delta E_x(\text{dens})$ reflects the fact that the LDA is missing important nonlocal contributions responsible for the cancellation of the self-interaction energy already on the nonrelativistic level. The much larger LDA error for $\Delta E_x(\text{fctl})$, on the other hand, directly shows
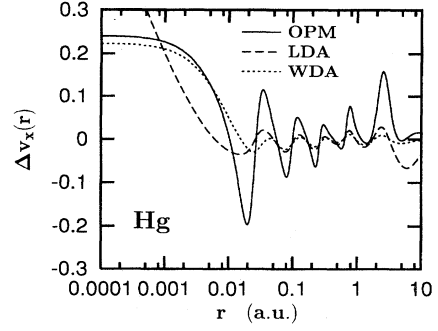

FIG. 3. Relativistic correction to the longitudinal x-only potential $\Delta v_x(r)$, Eq. (4.8), for neutral Hg from OPM, LDA, and WDA calculations [61].

that nonlocal corrections are even more relevant for the relativistic correction $E_x^L[n] - E_x^{\text{NR}}[n]$. Furthermore, the total LDA deviation of 3.922 hartree found for Hg^{78+} matches rather well with the deviation of 4.229 hartree for neutral Hg, suggesting that the major contribution to ΔE_x comes from the $1S_{1/2}$ electrons, while contributions of the order of 300 mhartree are due to the relativistic rearrangement of other orbitals.

The corresponding plots of $\Delta v_x(r)$ for Hg and Hg^{78+} are given in Figs. 3–5. In Fig. 3 one first of all observes an "oscillatory" behavior between 0.01 a.u. and 3 a.u. reflecting the shell structure of the atom: The relativistic single-particle orbitals are shifted towards the nucleus with respect to the nonrelativistic ones, resulting in an oscillating structure of $n^R(r) - n^{\text{NR}}(r)$ and thus also of the potential. Note that the relativistic correction in the exact v_x^L amounts to roughly 10% even in the valence regime. This shell oscillation is only partially reproduced by the RLDA, the OPM-amplitudes being larger by more than a factor of 2. Decomposing $\Delta v_x(r)$ into a density and a functional component [in analogy to Eqs. (4.10)–(4.12)],

$$\Delta v_x(r) = \Delta v_x(r, \text{dens}) + \Delta v_x(r, \text{fctl}), \qquad (4.13)$$

$$\Delta v_x(r, \text{dens}) = \frac{v_x^{\text{NR}}([n^R]; r) - v_x^{\text{NR}}([n^{\text{NR}}]; r)}{v_x^{\text{NROPM}}([n^{\text{NROPM}}]; r)}, \qquad (4.14)$$
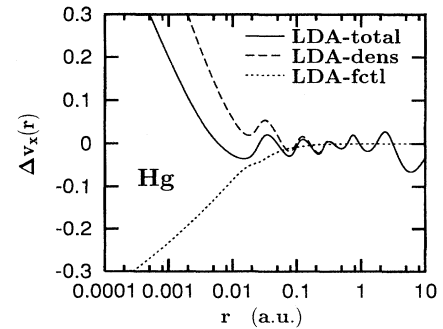

FIG. 4. Decomposition of Δv_x (total) into its density component (4.14) (dens) and the functional contribution (4.15) (fctl): LDA results for neutral Hg [61].
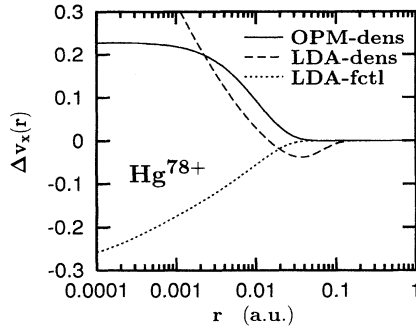
FIG. 5. Decomposition of $\Delta v_x(r)$ for Hg^{78+}: Exact $\Delta v_x(r,\text{dens})$ (OPM-dens) in comparison to $\Delta v_x^{\text{LDA}}(r,\text{dens})$ (LDA-dens) and $\Delta v_x^{\text{LDA}}(r,\text{fctl})$ (LDA-fctl) [61].

$$\Delta v_x(r,\text{fctl}) = \frac{v_x^L([n^R];r) - v_x^{NR}([n^R];r)}{v_x^{\text{NROPM}}([n^{\text{NROPM}}];r)}, \quad (4.15)$$

one finds that the oscillatory structure is completely due to the density correction $\Delta v_x(r,\text{dens})$, as can be gleaned from Fig. 4 [the LDA result for $\Delta v_x(r,\text{dens})$ is almost identical to the complete self-consistent $\Delta v_x(r)$ from the RNRLDA]. As to be expected the functional correction $\Delta v_x(r, \text{fctl})$ is only relevant for the high-density small-r regime, i.e., the innermost orbitals. In this regime, however, the $\Delta v_x(r)$ from the LDA is rather different from the exact OPM result. In order to demonstrate on a local basis that both components of $\Delta v_x(r)$ contribute to the LDA's error, it is again advantageous to consider Hg^{78+}: Similar to the situation for ΔE_x the exact $\Delta v_x(r,\text{fctl})$ vanishes. As is clear from Fig. 5 the LDA is far from reproducing the exact $\Delta v_x(r)$. In particular,

$|\Delta v_x^{\text{LDA}}(r,\text{fctl})|$ does not vanish but is of the same order of magnitude as the exact $\Delta v_x(r,\text{dens})$.

Consequently, the origin of the RLDA's deviation for neutral atoms is twofold: The error is dominated by the self-interaction of the $1S_{1/2}$ electrons which manifests itself mainly in the functional correction $E_x^L[n] - E_x^{\text{NR}}[n]$. The smaller (but chemically equally relevant) error in the density components $\Delta E_x(\text{dens})$ and $\Delta v_x(r,\text{dens})$, on the other hand, is a result of the LDA's difficulties to reproduce the shell structure of the exact $n^{\text{(R)OPM}}$ already in the nonrelativistic regime [40,22]: The amplitude (not the location) of the relativistic shift of the individual shells becomes larger the more pronounced the shells are. Thus while the first source of errors calls for improved, i.e., nonlocal, relativistic corrections to the x-only energy functional, the second problem can only be solved by using a more accurate nonrelativistic basis for $E_x^L[n]$ than the NRLDA in relativistic DF calculations. A number of concepts are available in the latter respect (like, e.g., GGA's), but we only address the question of improved relativistic corrections in this contribution (in Sec. IVB).

However, before further addressing this question, a few remarks on transverse exchange seem appropriate. The transverse x-only energies calculated from the self-consistent RLDA densities are compared to RHF results [58,38] in Table VI (note that the RHF orbitals used for these energies [38,58] could be replaced by the ROPM or RLDA orbitals without significantly changing the resulting E_x^T's: For Hg, e.g., one obtains 22.145 hartree by inserting the self-consistent RLDA orbitals into the transverse Fock term). As already recognized by MacDonald and Vosko [27] the RLDA overestimates the exact E_x^T by about a factor of 1.5. Moreover, in contrast to the RLDA's error for ΔE_x, its deviation for E_x^T does not decrease with increasing Z. Thus the RLDA

TABLE VI. Transverse exchange energy (E_x^T) from RHF [58,38] and RLDA calculations and its components. $E_x^{T,\text{mag}}$: current-current contribution; $E_x^{T,\text{ret}}$: photon retardation correction to density-density contribution; $E_x^{T,\text{Breit}}$: Breit approximation to E_x^T. Also given is the total correction $\Delta E_x + E_x^T$ [61] (all energies are in hartrees).

Atom	RHF					RLDA				
	E_x^T	$E_x^{T,\text{mag}}$	$-E_x^{T,\text{ret}}$	$E_x^{T,\text{Breit}}$	$\Delta E_x + E_x^T$	E_x^T	$E_x^{T,\text{mag}}$	$-E_x^{T,\text{ret}}$	$E_x^{T,\text{Breit}}$	$\Delta E_x + E_x^T$
He	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Be	0.001	0.001	0.000	0.001	0.000	0.002	0.002	0.000	0.002	0.001
Ne	0.017	0.018	0.001	0.017	0.002	0.035	0.042	0.007	0.035	0.028
Mg	0.032			0.032	0.003	0.065	0.078	0.013	0.064	0.050
Ar	0.132	0.143	0.011	0.132	0.014	0.249	0.300	0.050	0.248	0.180
Ca	0.191			0.191	0.019	0.353	0.425	0.072	0.352	0.249
Zn	0.759	0.834	0.075	0.761	0.131	1.322	1.595	0.272	1.312	0.920
Kr	1.419	1.566	0.146	1.427	0.203	2.401	2.901	0.500	2.373	1.586
Sr	1.710			1.720	0.231	2.867	3.467	0.600	2.831	1.862
Pd	3.290			3.318	0.503	5.358	6.501	1.143	5.263	3.399
Cd	3.808	4.218	0.410	3.842	0.541	6.162	7.484	1.321	6.045	3.840
Xe	5.711	6.331	0.621	5.775	0.687	9.089	11.071	1.982	8.877	5.431
Ba	6.473			6.552	0.733	10.255	12.505	2.250	10.001	6.038
Yb	13.897	15.393	1.496	14.148	1.846	21.557	26.521	4.964	20.778	12.355
Hg	22.166	24.503	2.335	22.665	2.192	34.201	42.412	8.212	32.654	18.444
Rn	28.676	31.647	2.966	29.397	2.028	44.313	55.265	10.952	42.046	22.964
Ra	31.148			31.957	1.899	48.202	60.240	12.039	45.636	24.638
No	53.576	58.759	5.158	55.248	1.154	84.987	108.154	23.167	79.083	41.085

can only serve as a qualitative measure of transverse x-only energies. Furthermore, due to the rather subtle cancellation between the exact ΔE_x and E_x^T, the RLDA completely misrepresents the total relativistic correction to atomic E_x's (see Table VI).

In Table VI also various components of E_x^T are listed (compare [32]). The magnetic, or current-current, contribution $E_x^{T,\mathrm{mag}}$ originates from the spatial components of $D_{\mu\nu}^{0,T}$, Eq. (2.12), while $E_x^{T,\,\mathrm{ret}}$ is due to $D_{00}^{0,T}$. Finally, expanding $D_{\mu\nu}^{0,T}$ to first order in $1/c^2$ leads to the Breit approximation $E_x^{T,\,\mathrm{Breit}}$. Both $E_x^{T,\mathrm{mag}}$ and in particular $E_x^{T,\mathrm{ret}}$ are grossly misrepresented by the RLDA. On the other hand, $E_x^{T,\mathrm{Breit}}$ is rather close to the full E_x^T throughout the periodic table for both RHF and the RLDA.

Lacking the transverse ROPM exchange potential, one has to resort to an indirect analysis of $v_x^{T,\mathrm{RLDA}}(r)$ based on the self-consistent orbitals φ_k^{L+T} obtained by including $v_x^{T,\mathrm{RLDA}}(r)$ in the RKS potential (2.14). In particular, one can use the difference between the $E_x^{T,\,\mathrm{Breit}}$ found by inserting these φ_k^{L+T} into the Breit Fock term and the $E_x^{T,\mathrm{Breit}}$ calculated with the φ_k corresponding to the purely longitudinal RKS potential (2.14) as a quantitative measure of $v_x^T(r)$. On the basis of RHF orbitals one finds for the fully self-consistent $E_x^{T,\mathrm{Breit}}$ of Hg 22.633 hartree [63], while a perturbative evaluation yields 22.665 [38]. The difference of 32 mhartree may now be compared to the difference of 153 mhartree between the $E_x^{T,\mathrm{Breit}}$ calculated from φ_k^{L+T} (22.483 hartree) and that from the longitudinal φ_k (22.636 hartree), indicating that the RLDA overestimates $v_x^T(r)$ drastically.

The failure of the RLDA in the case of $E_x^T[n]$ is, however, not surprising in view of its RHEG origin. The finite speed of light plays a much more important role for an infinite system like the RHEG than for atoms: In the RHEG extremely distant points in space are interacting with each other such that the traveling time of photons between these points modifies the form of the long range electromagnetic forces (similar to the difference between Casimir-Polder and van der Waals forces [64]). The electronic density of atoms, on the other hand, is rather localized so that the actual propagation of photons as compared to the instantaneous Coulomb interaction can not have the same impact.

B. Weighted-density approximation

Nonlocal x-only energy functionals can either be obtained by the derivation of systematic corrections to the LDA (e.g., in the form of gradient corrections) or, in a more phenomenological way, by making an *ad hoc* ansatz in which as much insight into the nature of the physical problem is incorporated as possible. Among the latter, one of the most prominent approaches is the WDA. The WDA explicitly addresses the problem of self-interaction so that it appears particularly attractive in the present situation. In complete analogy to the nonrelativistic case the relativistic x-only WDA is based on the (exact) representation of the longitudinal x-only energy [31,36,65],

$$E_x^L = \frac{e^2}{2}\int d^3x \int d^3y \; \frac{n(x)n(y)[g_x(x,y)-1]}{|x-y|}, \quad (4.16)$$

in terms of the noninteracting (or x-only) limit $g_x(x,y)$ of the pair correlation function,

$$g(x,y) = \frac{\langle\Phi_0|\hat{n}(x)\hat{n}(y)|\Phi_0\rangle}{n(x)n(y)} - \frac{\delta^{(3)}(x-y)}{n(x)}. \quad (4.17)$$

The exact $g(x,y)$ as well as the exact $g_x(x,y)$ satisfy the sum rule

$$\int d^3y\, n(y)[g_x(x,y)-1] = -1. \quad (4.18)$$

By contrast, local-density-functional approximations to $g_x(x,y)$ will no longer satisfy (4.18). The central idea of the WDA [5,6] is to go beyond the LDA by enforcing (4.18) also for suitable approximations to $g_x(x,y)$. While in the nonrelativistic case a number of qualitatively different model pair correlation functions have been suggested [53–56] for this purpose, a systematic relativistic extension is only available for the most simple $g_x(x,y)$, i.e., the pair correlation function of the HEG. While the nonrelativistic $g_x^{\mathrm{HEG}}(x,y)$ is a function of $z = k_F|x-y|$ only,

$$g_x^{\mathrm{HEG}}(z) = 1 - \frac{9}{2}\left[\frac{j_1(z)}{z}\right]^2, \quad (4.19)$$

the pair correlation function of the RHEG [24,27],

$$g_x^{\mathrm{RHEG}}(z,k_F) = 1 - \frac{9}{4}\left[\frac{1}{\eta^2}\left(\sum_{i=0}^{\infty}\frac{j_{i+1}(z)}{z^{i+1}}\left(\frac{\beta}{\eta}\right)^{2i}\frac{(2i+1)!!}{2i+1}\right)^2\right.$$
$$+ \frac{\beta^2}{\eta^2}\left(\sum_{i=0}^{\infty}\frac{j_{i+2}(z)}{z^{i+1}}\left(\frac{\beta}{\eta}\right)^{2i}\frac{(2i+1)!!}{2i+1}\right)^2$$
$$\left. + \left(\frac{j_1(z)}{z}\right)^2\right] \quad (4.20)$$

also depends on k_F separately. For an inhomogeneous system the Fermi momentum k_F is now replaced by a local screening momentum $\tilde{k}_F(x)$ which is chosen such that $g_x^{\mathrm{RHEG}}(\tilde{k}_F(x)|x-y|,\tilde{k}_F(x))$ satisfies Eq. (4.18) with the actual density $n(y)$. The x-only energy functional is then given by

$$E_x^{L,\mathrm{RWDA}}[n] = \frac{e^2}{2}\int d^3x \int d^3y\, \frac{n(x)n(y)}{|x-y|}$$
$$\times [g_x^{\mathrm{RHEG}}(\tilde{k}_F(x)|x-y|,\tilde{k}_F(x))-1].$$
$$(4.21)$$

The main advantage of this approximation is that it is exact for two-electron systems [if the correct $\tilde{k}_F(x)$ is utilized in (4.21) before performing the functional differentiation (2.16)] and also correctly accounts for the self-interaction energies of individual closed shells if a shell-partitioning scheme is used [66]. Furthermore, the WDA reproduces the asymptotic r^{-1} behavior of the exact x-only potential (although with the incorrect prefactor of $1/2$ [67]).

Unfortunately, the nonrelativistic WDA with g_x^{HEG} as kernel substantially overestimates atomic exchange energies [5] and completey misrepresents the corresponding exchange potentials [68]. This deficiency of the WDA, however, is not

TABLE VII. Comparison of CI and second-order MBPT correlation energies with LDA results. $E_{c,2}^{NRCI}$: second-order MBPT for nonrelativistic CI correlation energy [63]; E_c^{NRCI}: nonrelativistic CI correlation energy from CI calculations [70,71]; $E_c^{(NR)CI}$: CI correlation energy estimated from both nonrelativistic CI calculations and experimental ionization potentials [71]; E_c^{NRLDA}: LDA result for nonrelativistic DFT correlation energy; $\Delta E_{c,2}^{CI}$: second-order MBPT for ΔE_c [63]; ΔE_c^{LDA}: LDA result for ΔE_c; $E_{c,2}^{T,RCI}$: Breit contribution to second-order MBPT for E_c^T [63]; $E_c^{T,RLDA}$: RLDA result for E_c^T [61] (all energies are in hartrees).

Atom	$-E_{c,2}^{NRCI}$	$-E_c^{NRCI}$	$-E_c^{(NR)CI}$	$-E_c^{NRLDA}$	$-\Delta E_{c,2}^{CI}$	$-\Delta E_c^{LDA}$	$-E_{c,2}^{T,RCI}$	$-E_c^{T,RLDA}$
He	0.037	0.042	0.042	0.111	0.000	0.000	0.000	0.000
Be		0.094	0.094	0.224		0.000		0.000
Ne	0.383	0.386	0.390	0.743	0.000	0.000	0.002	0.000
Mg			0.438	0.891		0.001		0.001
Ar	0.697		0.722	1.430	0.001	0.003	0.008	0.002
Zn	1.651			2.665	0.011	0.011	0.026	0.008
Kr	1.835			3.283	0.011	0.020	0.041	0.013
Cd	2.618			4.571	0.036	0.045	0.082	0.029
Xe	2.921			5.200	0.038	0.065	0.109	0.039
Hg	5.086			8.356	0.203	0.201	0.283	0.113
Rn	5.392			9.027	0.195	0.257	0.353	0.138

transferred to the relativistic corrections ΔE_x and $\Delta v_x(r)$, as is shown in Table V and Fig. 3. [Note that for our actual calculations an accurate approximation to g_x^{RHEG}, Eq. (4.20), has been used — see the Appendix.] In fact, although the ΔE_x obtained in the WDA also exhibit some tendency to overestimate the exact values, the WDA is more accurate than the local approximations RLDA and RNRLDA. In particular, one would expect the remaining error to be mainly due to the ΔE_x(dens) component as the ΔE_x(fctl) from the RWDA correctly vanishes for all two-electron systems. Also, the $\Delta v_x(r)$ from the WDA are close to the exact results in the small-r regime as demonstrated for neutral Hg in Fig. 3, emphasizing the accurate description of $\Delta v_x(r,fctl)$ by the WDA. As is to be expected from the physical nature of the relativistic effects in $E_x^L[n]$ the concept of the WDA seems very suitable as a basis for nonlocal x-only functionals. This result calls for a relativistic extension of one of those model pair correlation functions which are more accurate than $g_x^{(R)\ HEG}$ in the nonrelativistic regime. Such an extension could, e.g., be based on a scaling approach similar to that utilized in the Appendix.

V. LOCAL-DENSITY APPROXIMATION TO THE RELATIVISTIC CORRELATION ENERGY FUNCTIONAL

The relativistic correlation energy functional $E_c[n]$ is defined on the basis of the x-only energy functional, Eq. (3.1),

$$E_c^{L/T}[n] = E_{xc}^{L/T}[n] - E_x^{L/T}[n], \tag{5.1}$$

where again a decomposition into a longitudinal and a transverse part is possible. As for the x-only energy the LDA is the natural approximation to start with in the case of $E_c[n]$. While, unlike the nonrelativistic case, no Monte Carlo evaluation of the correlation energy of the RHEG is available to date, fortunately only its high-density limit is of interest in the present context. The relevant ring diagram contributions are given by [50,52,31],

$$e_c^{L,RPA}(n_0) = -\frac{i}{2} \int \frac{d^4q}{(2\pi)^4} \left\{ \ln\left[1 + \frac{4\pi e^2 \Pi^L(q)}{q^2} \right] - \frac{4\pi e^2 \Pi^L(q)}{q^2} \right\}, \tag{5.2}$$

$$e_c^{T,RPA}(n_0) = -i \int \frac{d^4q}{(2\pi)^4} \left\{ \ln\left[1 - \frac{4\pi e^2 \Pi^T(q)}{q^2} \right] + \frac{4\pi e^2 \Pi^T(q)}{q^2} \right\}, \tag{5.3}$$

where $\Pi^L(q)$ and $\Pi^T(q)$ represent the longitudinal and transverse components of the noninteracting relativistic current-current response function. The integrals (5.2) and (5.3) have been evaluated by Ramana and Rajagopal [31] and, more recently, by Müller and Serot [57], whose very accurate results are used here (for plots of $e_c^{L/T,RPA}$ see Refs. [31,36]). The resulting $E_c^{L/T,RPA}[n]$,

$$E_c^{L/T,RPA}[n] = \int d^3r\, e_c^{L/T,RPA}(n), \tag{5.4}$$

has been applied to the correlation energies of high-Z atoms by Ramana and Rajagopal [31] and Ramana, Rajagopal and Johnson [31,32]. Unfortunately, the RPA is not an accurate approximation to the correlation energy of the HEG, in particular for intermediate and low densities [69]. In order to establish a more complete relativistic LDA we thus combine the relativistic RPA (RRPA) with its nonrelativistic counterpart (NRRPA) and the complete nonrelativistic LDA (NRLDA),

$$E_c^{L,RLDA}[n] = E_c^{L,RRPA}[n] - E_c^{NRRPA}[n] + E_c^{NRLDA}[n], \tag{5.5}$$

i.e., we only utilize the relativistic correction provided by the RPA, while for nonrelativistic densities the complete NRLDA is used (with the parametrization of Vosko et al. [69]). Thus for high densities $E_c^{NRRPA}[n]$ and $E_c^{NRLDA}[n]$ essentially cancel so that $E_c^{L,RLDA}[n] = E_c^{L,RRPA}[n]$, while for

TABLE VIII. Comparison of CI and second-order MBPT correlation energies with RLDA results for two-electron systems. $E_{c,2}^{\mathrm{NRCI}}$: second-order MBPT for nonrelativistic CI correlation energy [76]; E_c^{NRCI}: nonrelativistic CI correlation energy from CI calculations [70,71]; E_c^{NRLDA}: LDA result for nonrelativistic DFT correlation energy; $\Delta E_{c,2}^{\mathrm{CI}}$: second-order MBPT for ΔE_c [76]; $\Delta E_c^{\mathrm{LDA}}$: LDA result for ΔE_c; $E_{c,2}^{T,\mathrm{RCI}}$: Breit contribution to second-order MBPT for E_c^T [76]; $E_c^{T,\mathrm{RLDA}}$: RLDA result for E_c^T [61] (all energies are in mhartree).

Ion	$-E_{c,2}^{\mathrm{NRCI}}$	$-E_c^{\mathrm{NRCI}}$	$-E_c^{\mathrm{NRLDA}}$	$-\Delta E_{c,2}^{\mathrm{CI}}$	$-\Delta E_c^{\mathrm{LDA}}$	$-E_{c,2}^{T,\mathrm{RCI}}$	$-E_c^{T,\mathrm{RLDA}}$
He	37.135	42.044	111.469	-0.003	0.000	0.037	0.000
Be^{2+}		44.267	150.462		0.010		0.017
Ne^{8+}	44.368	45.693	202.680	-0.074	0.267	1.398	0.274
Mg^{10+}		45.854	213.233		0.456		0.450
Ar^{16+}		46.123	236.903		1.413		1.305
Ca^{18+}	45.374	46.177	243.098	-0.194	1.874	5.695	1.705
Zn^{28+}	45.710		267.099	-0.193	5.413	12.635	4.614
Zr^{38+}	45.876		284.270	0.060	11.294	22.113	9.012
Sn^{48+}	45.976		297.662	0.685	19.921	34.190	14.837
Hg^{78+}			326.051		68.372		41.107

low densities $E_c^{L,\mathrm{RRPA}}[n]$ and $E_c^{\mathrm{NRRPA}}[n]$ are identical. Note that the scheme (5.5) could be used with more accurate ingredients.

The results from (5.5) for a number of (spherical) atoms are summarized in Table VII and compared to the usual quantum chemical correlation energy E_c^{RCI},

$$E_c^{\mathrm{RCI}} = E_{\mathrm{tot}} - E_{\mathrm{tot}}^{\mathrm{RHF}} - \Delta E^{\mathrm{QED}}. \qquad (5.6)$$

Here the RHF ground state energy $E_{\mathrm{tot}}^{\mathrm{RHF}}$ includes the transverse energy contributions as well as the finite nuclear size correction and ΔE^{QED} represents all quantum-electrodynamical corrections (when extracting E_{tot} from experimental data also the finite nuclear mass has to be taken into account [70]). Consequently E_c^{RCI} contains all relativistic corrections to the correlation energy. Unfortunately, apart from the two-electron systems, $E_{\mathrm{tot}}^{\mathrm{RHF}}$ is not identical to the corresponding ROPM ground state energy so that the exact density functional E_c does not exactly agree with E_c^{RCI} but is somewhat larger in magnitude. This small difference, however, is irrelevant for the present purpose, so we use E_c^{RCI} as a reference standard. The same holds for the nonrelativistic quantum chemical correlation energy,

$$E_c^{\mathrm{NRCI}} = E_{\mathrm{tot}}^{\mathrm{NR}} - E_{\mathrm{tot}}^{\mathrm{HF}}, \qquad (5.7)$$

with respect to the nonrelativistic E_c.

An idea of the uncertainty of currently available atomic E_c^{NRCI}'s is obtained by comparing the purely theoretical state-of-the-art values given in [70,71] with the results obtained by combining very accurate nonrelativistic CI calculations for two- and three-electron systems with experimental information on atomic ions with more than three electrons [71] (called $E_c^{(\mathrm{NR})\mathrm{CI}}$ in Table VII). As a matter of principle, the latter values neither agree with the nonrelativistic nor with the relativistic CI correlation energies as the experimental data utilized in [71] have not been corrected for relativistic contributions to E_c. Thus the difference between the theoretical and the empirical result for Ne of 4 mhartree reflects both the limitations of present CI calculations (compare [72,43,73]) and a small fraction of the relativistic corrections

to E_c^{NRCI}. Nevertheless this uncertainty is sufficiently small to allow the use of $E_c^{(\mathrm{NR})\mathrm{CI}}$ as nonrelativistic reference standard.

As is well known the LDA overestimates the exact atomic correlation energies by about a factor of 2. Here, however, it is not so much the accuracy of the complete functional (5.5) which is of interest but rather the relativistic correction to the longitudinal correlation energy E_c^L,

$$\Delta E_c = E_c^L[n^R] - E_c^{\mathrm{NR}}[n^{\mathrm{NR}}], \qquad (5.8)$$

and the transverse correlation energy E_c^T as the RRPA could be combined with more accurate nonrelativistic $E_c[n]$. Table VII shows that both ΔE_c and E_c^T are much smaller than their x-only counterparts. This conclusion is not really changed by the fact that ΔE_c and E_c^T add up constructively so that the total correction $\Delta E_c + E_c^T$ is not as much smaller than $\Delta E_x + E_x^T$ as the individual components: For neutral Hg one obtains $\Delta E_c + E_c^T = -0.49$ hartree within second-order MBPT compared to the exact $\Delta E_x + E_x^T$ of about 2.19 hartree. Thus relativistic corrections to $E_c[n]$ are less important than those to $E_x[n]$. This is also obvious from the $1S_{1/2}$ eigenvalues which reflect the role of the relativistic contributions in the correlation potential $v_c^L([n];r)$: For Hg the shift induced in $\epsilon_{1S1/2}$ by going from $v_c^{\mathrm{NRLDA}}([n],r)$ to $v_c^{\mathrm{RLDA}}([n];r)$ amounts to 56 mhartree as compared to -3.107 hartree in the case of exchange (see Table III).

Lacking the corresponding full RCI-results we resort to second-order many-body perturbation theory (MBPT) [63] in order to judge the accuracy of $\Delta E_c^{\mathrm{RLDA}}$ and $E_c^{T,\mathrm{RLDA}}$. As has been discussed in Ref. [63] for Xe and is also obvious from Table VII for small Z the second-order MBPT results reproduce the full CI values within about 5%, which is completely sufficient for the present purpose. Two features are immediately clear from Table VII: On the one hand, $\Delta E_{c,2}$ and $E_{c,2}^T$ do not increase with Z as smoothly as the corresponding RLDA results. On the other hand, while the RLDA for $\Delta E_{c,2}$ agrees with the second-order MBPT values at least for some atoms, the size of $E_{c,2}^T$ cannot be reproduced by the RLDA. The RLDA's overall relative error for ΔE_c and E_c^T is even larger than that for ΔE_x and E_x^T.
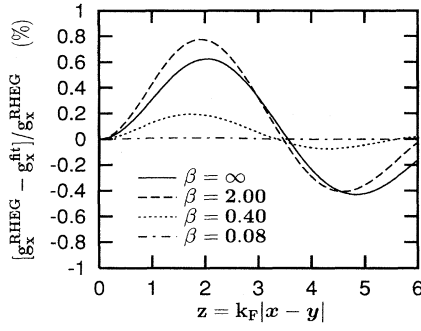
FIG. 6. Percentage deviation of $g_x^{\text{fit}}(z,\beta)$, Eq. (A5), from the exact $g_x^{\text{RHEG}}(z,\beta)$, Eq. (4.20), as a function of z for various values of β.

Moreover, the RLDA also does not reproduce the almost Z-independent longitudinal correlation energy observed for two-electron systems ([74,75]; compare Table VIII): While for He the RLDA overestimates the exact E_c^L by about a factor of 2.5, for Hg^{78+} the RLDA result of $E_c^L = 394$ mhartree is already larger than the CI value of roughly 43 mhartree [75] by almost an order of magnitude. In particular, the relativistic contribution ΔE_c is grossly misrepresented by the LDA in the case of two-electron systems: For Sn^{48+} the LDA result of 19.9 mhartree may be compared with the second-order MBPT value of 0.69 mhartree [76]. On the other hand, E_c^T is markedly underestimated by the RLDA. The agreement between the total relativistic correction $\Delta E_c + E_c^T$ from the LDA and the corresponding MBPT value in the regime $Z \approx 50$ must thus be regarded as fortuitous.

In summary, the RLDA addresses relativistic corrections to $E_c[n]$ on the same limited level of sophistication as the NRLDA does for the nonrelativistic correlation energy functional. Even more than in the case of exchange, nonlocal corrections seem to be required for a really satisfying description of (relativistic) correlation effects in atoms.

VI. CONCLUDING REMARKS

The RLDA for the longitudinal exchange-correlation energy functional is not found to be fully adequate, the main reason being the failure of the RLDA to reproduce the correct interplay between relativistic and self-interaction effects. Part of the problems with the RLDA originate from the nonrelativistic regime so that these errors can be reduced by adding nonrelativistic nonlocal corrections (as, e.g., gradient terms) [77]. The remaining errors (in the so-called functional correction — see Sec. IV), however, require intrinsically relativistic nonlocal corrections.

At present essentially two concepts addressing this issue are conceivable: On the one hand, a relativistic gradient correction (to be derived from the linear response function of the RHEG [36]) could serve as basis for a relativistic generalized gradient approximation. An interesting alternative might be provided by the relativistic WDA. In fact, the case of the longitudinal exchange energy functional has indicated the potential strength of this approach. Further improvement

might be expected if the rather simple relativistic exchange-only pair correlation function used in the present study is replaced by a more adequate form.

Alternatively, one could try to utilitze the advantages of the WDA at the present stage by combining it with an accurate nonrelativistic x-only functional, $E_x^{\text{NRA}}[n]$ (like a generalized gradient approximations [19,20,22]) in a pragmatic way,

$$E_x^{L,\text{RA}}[n] = E_x^{L,\text{RWDA}}[n] - E_x^{\text{NRWDA}}[n] + E_x^{\text{NRA}}[n].$$

The main idea of this construction is to eliminate the error of the WDA for the nonrelativistic low-density regime by only including the functional correction $E_x^L[n] - E_x^{NR}[n]$ in the form of the WDA. Thus $E_x^{\text{NRA}}[n]$ is dominating $E_x^{L,\text{RA}}[n]$ for nonrelativistic densities, while the WDA is "switched on" in the high-density regime. Correlation contributions could be treated analogously, using a correlated pair correlation function.

As far as transverse (or Breit) contributions are concerned the RLDA seems to be less adequate. Whether the addition of gradient corrections or a WDA scheme based on the Breit interaction can remedy this situation remains to be investigated.

ACKNOWLEDGMENTS

APPENDIX: SIMPLE ANALYTIC APPROXIMATION FOR THE PAIR CORRELATION FUNCTION OF THE RELATIVISTIC HOMOGENEOUS ELECTRON GAS

The series representation (4.20) of the x-only pair correlation function of the RHEG is not very suitable for actual applications of the RWDA. We have thus developed a simple and accurate fit to g_x^{RHEG} which might also be useful for other purposes. It is based on the form of $g_x^{\text{RHEG}}(z,k_F)$ for $z = 0$,

$$g_x^{\text{RHEG}}(0,k_F) = \frac{3}{4} - \frac{9}{16}\left[\frac{\eta}{\beta^2} - \frac{\text{arcsinh}(\beta)}{\beta^3}\right]^2, \quad \text{(A1)}$$

with the limits

$$\lim_{\beta \to 0} g_x^{\text{RHEG}}(0,k_F) = \frac{1}{2}, \quad \text{(A2)}$$

$$\lim_{\beta \to \infty} g_x^{\text{RHEG}}(0,k_F) = \frac{3}{4}. \quad \text{(A3)}$$

Equation (A3) may be interpreted as a consequence of the relativistic mixing of spin states [24]. The decreasing depth of the exchange hole $g_x^{\text{RHEG}} - 1$ with increasing β apparent from (A2) and (A3) is compensated by a broadening of the "width" of the exchange hole (compare [24,27]) in order to satisfy (4.18) in the homogeneous limit,

$$\frac{4}{3\pi}\int_0^\infty z^2 dz \ [g_x^{RHEG}(z,k_F)-1]=-1. \qquad (A4)$$

The scaling behavior required for (A4) suggests the ansatz

$$g_x^{fit}(z,k_F)=1-\frac{9}{2}\,C_1(\beta)\left[\frac{j_1(C_2(\beta)z)}{C_2(\beta)z}\right]^2, \qquad (A5)$$

$$C_1(\beta)=\frac{1}{2}+\frac{9}{8}\left[\frac{\eta}{\beta^2}-\frac{arcsinh(\beta)}{\beta^3}\right]^2, \qquad (A6)$$

$$C_2(\beta)=[C_1(\beta)]^{1/3}, \qquad (A7)$$

which not only approaches the correct nonrelativistic $g_x^{HEG}(z)$, Eq. (4.19), for vanishing β,

$g_x^{fit}(z,k_F)\underset{\beta\to 0}{\longrightarrow} g_x^{HEG}(z)$, but also satisfies Eqs. (A1) and (A4).

The percentage deviation of $g_x^{fit}(z,k_F)$ from $g_x^{RHEG}(z,k_F)$ is plotted in Fig. 6. In fact, even in the limit $\beta\to\infty$ in which

$$g_x^{RHEG}(z,\infty)=1-\frac{9}{4}\left[\left(2\frac{j_1(z)}{z^2}-\frac{j_0(z)}{z^3}(2+z^2)+\frac{2}{z^3}\right)^2 \right.$$
$$\left. +\left(\frac{j_1(z)}{z^2}\right)^2\right], \qquad (A8)$$

the error does not exceed 1%, while for the more relevant moderately high densities ($\beta<0.5$ — at the r-expectation value of Hg^{78+} one finds $\beta=0.6$) the error reduces to less than 0.2%.

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in the nonrelativistic KS equations. If a nonrelativistic x(c) functional is used in the relativistic KS equations the resulting scheme is characterized by RNR (e.g., RNRLDA abbreviates the Dirac-Fock-Slater approach with $\alpha = 2/3$, i.e., using the nonrelativistic LDA functional in the relativistic KS equations). Finally, all differences between relativistic and nonrelativistic results are referenced by the generic name of the approximation, e.g., LDA.

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[61] In all our calculations the nuclei were represented by uniformly charged spheres with nuclear radii given by $R_{\rm nucl} = 1.0793\, A^{1/3} + 0.735\,87$ fm, A being the atomic mass (weighted by isotopic abundances) taken from Table III.7 of K. Hikasa *et al.* (Particle Data Group), Phys. Rev. D **45**, S1 (1992), unless explicitly stated otherwise. The speed of light had been set to $c = 137.035\,989\,5$.

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