Approximate relativistic optimized potential method

T. Kreibich and E. K. U. Gross
Institut für Theoretische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

E. Engel
Institut für Theoretische Physik, Universität Frankfurt, Robert Mayer Straße 8-10, D-60054 Frankfurt-am-Main, Germany

(Received 28 July 1997)

Approximate semianalytical solutions of the integral equation for the relativistic optimized potential are constructed by extending a method recently proposed by Krieger, Li, and Iafrate [Phys. Lett. A **146**, 256 (1990)] to the relativistic regime. The quality of the approximation is tested in the longitudinal x-only limit where fully numerical solutions of the relativistic optimized effective potential integral equation are available for spherical atoms. The results obtained turn out to be in excellent agreement with the exact x-only values. The proposed method provides significant improvement over the conventional relativistic local density approximation and generalized gradient approximation schemes. [S1050-2947(97)04912-3]

PACS number(s): 31.10.+z, 71.10.−w, 31.30.Jv, 31.15.Ew

I. INTRODUCTION

Since the seminal work of Hohenberg and Kohn [1] and Kohn and Sham [2], density functional theory (DFT) has become a powerful tool for *ab initio* electronic structure calculations of atoms, molecules, and solids [3–5]. The development of more and more refined approximations of the exchange-correlation (xc) energy functional $E_{\rm xc}$ has led to significant improvement over the standard local density approximation (LDA). In particular, the so-called optimized potential method (OPM) [6,7] employing explicitly orbital-dependent functionals rather than the traditional density-dependent functionals has achieved highly accurate results [7–20].

Most of the advances in DFT have been made in the context of nonrelativistic physics. For high-Z atoms, however, relativistic contributions have to be considered. For example, the ground-state energy of mercury (Hg) decreases from its nonrelativistic value $-18\,408$ a.u. to $-19\,649$ a.u. if relativistic effects are taken into account. Furthermore, even for systems with moderate Z, relativistic contributions to $E_{\rm xc}$ are larger than the differences between the currently best xc energy functionals [21]. Until now, the calculation of such relativistic contributions has mostly been based on the relativistic local density approximation (RLDA). To go beyond the RLDA, an x-only version of the OPM was formulated for relativistic systems [22,21]. As in the nonrelativistic case, the solution of the resulting equations is a rather demanding task and has been achieved so far only for systems of high symmetry, e.g., spherical atoms [21,23–25].

The purpose of the present paper is to develop a simplified version of the relativistic OPM (ROPM) scheme leading to a generalization of the approximation of Krieger, Li, and Iafrate (KLI) [8–10,26–36] to the realm of relativistic systems. This will be done for systems subject to arbitrary static external four-potentials. The paper is organized as follows. In Sec. II we give a brief review of the foundations of relativistic DFT (RDFT). After that, in Sec. III, we develop the ROPM generalizing a nonrelativistic derivation of Görling and Levy [37] to the relativistic domain. The relativistic KLI (RKLI) scheme is developed in Sec. IV before some limiting cases are discussed in Sec. V. In Sec. VI, numerical results of the ROPM and RKLI methods are presented and compared to other RDFT methods.

II. THEORETICAL BACKGROUND

On its most general level, RDFT is based on quantum electrodynamics (QED) and thus contains not only relativistic but also radiative effects. For a detailed derivation, also including questions of renormalization, the reader is referred to recent reviews [23,38]. The central statement of RDFT — the relativistic version of the Hohenberg-Kohn (HK) theorem [39] — can be stated in the following way: The renormalized ground-state four-current $j^\nu(\mathbf{r})$ of an interacting system of Dirac particles uniquely determines, up to gauge transformations, the external four-potential $A^\mu_{\rm ext}[j^\nu]$ as well as the ground-state wave function $\Psi[j^\nu]$. As a consequence, any observable of the relativistic many-body system under consideration is a functional of its ground-state four-current. As in the nonrelativistic case, the exact ground-state four-current including all quantum electrodynamical effects can in principle be obtained from an auxiliary noninteracting system—the relativistic Kohn-Sham (RKS) system [21,38,40,41]:

$$j^\nu(\mathbf{r}) = \sum_{-c^2<\varepsilon_k\leq\varepsilon_F} \overline{\varphi_k}(\mathbf{r})\,\gamma^\nu\varphi_k(\mathbf{r}) + j^\nu_V(\mathbf{r}), \tag{1}$$

where $j^\nu_V(\mathbf{r})$ denotes the vacuum contribution to the four-current. The four-component spinors $\varphi_k(\mathbf{r})$ are solutions of an effective single-particle Dirac equation (in atomic units $\hbar = e = m = 1$)

$$\gamma_0\left[-ic\boldsymbol{\gamma}\cdot\nabla + c^2 + \gamma_\mu A^\mu_S[j^\nu](\mathbf{r})\right]\varphi_k(\mathbf{r}) = \varepsilon_k\varphi_k(\mathbf{r}), \tag{2}$$

with $A^\mu_S[j^\nu](\mathbf{r})$ being the effective four-potential, which can be decomposed according to

$$A^\mu_S[j^\nu](\mathbf{r}) = A^\mu_{\rm ext}(\mathbf{r}) + \int d^3r'\,\frac{j^\mu(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + A^\mu_{\rm xc}[j^\nu](\mathbf{r}). \tag{3}$$

Here, $A^{\mu}_{\rm ext}(\mathbf{r})$ is a static but otherwise arbitrary external four-potential, the second term on the right-hand side represents a Hartree-like potential, and the last term, defined by

$$A^{\mu}_{\rm xc}[j^{\nu}](\mathbf{r}) := \frac{\delta E_{\rm xc}[j^{\nu}]}{\delta j_{\mu}(\mathbf{r})} \tag{4}$$

denotes the xc four-potential containing by construction all nontrivial many-body effects.

Equations (1)–(4) represent the relativistic KS scheme that has to be solved self-consistently. However, the calculation of the vacuum contribution $j^{\nu}_{V}(\mathbf{r})$ to the four-current requires the knowledge of an infinite number of (positive and negative energy) states, so that one would have to deal with an infinite system of coupled equations. Since such a procedure is highly impractical, we will, in the following, ignore all vacuum contributions to the various energy components and to the four-current, which is then given just by the first term on the right-hand side of Eq. (1). This means that we restrict ourselves to the calculation of relativistic effects and neglect radiative corrections. Since we are aiming at electronic structure calculations for atoms, molecules, and solids, we expect the neglected terms to be small. If one were after all interested in the radiative contributions, an *a posteriori* perturbative treatment should be sufficient and represents in fact the standard approach.

III. RELATIVISTIC OPTIMIZED POTENTIAL METHOD

In order to derive a relativistic generalization of the OPM integral equation, we start out from the total-energy functional of a system of interacting Dirac particles (neglecting vacuum contributions) subject to a static external four-potential $A^{\mu}_{\rm ext}(\mathbf{r})$:

$$\begin{aligned} E^{\rm ROPM}_{\rm tot}[j^{\nu}] = & \sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F} \int d^3r\, \overline{\varphi_k}(\mathbf{r})(-ic\boldsymbol{\gamma}\cdot\nabla + c^2)\varphi_k(\mathbf{r}) \\ & + \int d^3r\, j_{\mu}(\mathbf{r}) A^{\mu}_{\rm ext}(\mathbf{r}) \\ & + \frac{1}{2}\int d^3r \int d^3r'\, \frac{j_{\mu}(\mathbf{r}) j^{\mu}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E^{\rm ROPM}_{\rm xc}[\{\varphi_i\}]. \end{aligned} \tag{5}$$

In contrast to the ordinary RDFT approach, the xc energy functional is given here as an explicit functional of the RKS four-spinors $\{\varphi_i\}$. Still, $E^{\rm ROPM}_{\rm xc}[\{\varphi_i\}]$ represents a functional of the density: Via the HK theorem applied to noninteracting systems, $j^{\nu}(\mathbf{r})$ uniquely determines the effective potential $A^{\mu}_{S}[j^{\nu}]$. With this very potential, the Dirac equation (2) is solved to obtain the set of single-particle orbitals $\{\varphi_i[j^{\nu}]\}$ which are then used to calculate the quantity $E^{\rm ROPM}_{\rm xc}[\{\varphi_i[j^{\nu}]\}]$. Therefore every functional, depending *explicitly* on RKS spinors, is an *implicit* functional of the density, provided the orbitals come from a local potential. This allows us to use the exact expression for the longitudinal exchange energy, i.e., the relativistic Fock term

$$\begin{aligned} E^{L,\rm exact}_{x}[j^{\nu}] = & -\frac{1}{2}\sum_{-c^2<\varepsilon_l,\varepsilon_k\leqslant\varepsilon_F} \int d^3r \int d^3r' \\ & \times \frac{\varphi^{+}_{l}(\mathbf{r})\varphi_k(\mathbf{r})\varphi^{+}_{k}(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \end{aligned} \tag{6}$$

One major advantage of such an exact treatment of the exchange energy lies in the fact that the spurious self-interactions contained in the Hartree energy are fully canceled. The price to be paid for the orbital dependence of $E_{\rm xc}$ is that the calculation of the xc four-potential $A^{\mu}_{\rm xc}(\mathbf{r})$, defined by Eq. (4), is somewhat more complicated. It has to be determined by an integral equation, as will be shown in the following.

Starting from the definition of $A^{\mu}_{\rm xc}(\mathbf{r})$, Eq. (4), we can calculate the xc four-potential corresponding to an orbital-dependent xc energy functional by applying the chain rule for functional derviatives:

$$\begin{aligned} A^{\rm ROPM}_{{\rm xc}\mu}(\mathbf{r}) = & \sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F} \int d^3r' \int d^3r'' \\ & \times \left(\frac{\delta E^{\rm ROPM}_{\rm xc}[\{\varphi_i\}]}{\delta\varphi_k(\mathbf{r}')} \frac{\delta\varphi_k(\mathbf{r}')}{\delta A_{S\nu}(\mathbf{r}'')} + \text{c.c.} \right) \frac{\delta A_{S\nu}(\mathbf{r}'')}{\delta j^{\mu}(\mathbf{r})}. \end{aligned} \tag{7}$$

The last term on the right-hand side of Eq. (7) is readily identified with the inverse of the static response function of a system of noninteracting Dirac particles

$$\chi^{\mu\nu}_{S}(\mathbf{r},\mathbf{r}') := \frac{\delta j^{\mu}(\mathbf{r})}{\delta A_{S\nu}(\mathbf{r}')}, \tag{8}$$

so that Eq. (9) can be rewritten as

$$\begin{aligned} A^{\rm ROPM}_{{\rm xc}\mu}(\mathbf{r}) = & \sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F} \int d^3r' \int d^3r'' \\ & \times \left(\frac{\delta E^{\rm ROPM}_{\rm xc}[\{\varphi_i\}]}{\delta\varphi_k(\mathbf{r}')} \frac{\delta\varphi_k(\mathbf{r}')}{\delta A_{S\nu}(\mathbf{r}'')} + \text{c.c.} \right) \chi^{-1}_{S\nu\mu}(\mathbf{r}'',\mathbf{r}). \end{aligned} \tag{9}$$

Acting with the response operator (8) on Eq. (9) and using the identity

$$\int d^3r\, \chi^{-1}_{S\nu\mu}(\mathbf{r}'',\mathbf{r}) \chi^{\mu\sigma}_{S}(\mathbf{r},\mathbf{r}') = \delta_{\nu}{}^{\sigma}\delta(\mathbf{r}''-\mathbf{r}') \tag{10}$$

we obtain (after rearranging the indices)

$$\begin{aligned} & \int d^3r'\, A^{\rm ROPM}_{{\rm xc}\nu}(\mathbf{r}') \chi^{\nu\mu}_{S}(\mathbf{r}',\mathbf{r}) \\ & = \sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F} \int d^3r' \frac{\delta E^{\rm ROPM}_{\rm xc}[\{\varphi_i\}]}{\delta\varphi_k(\mathbf{r}')} \frac{\delta\varphi_k(\mathbf{r}')}{\delta A_{S\mu}(\mathbf{r})} + \text{c.c.} \end{aligned} \tag{11}$$

To further evaluate this equation, we note that the first functional derivative on the right-hand side of Eq. (11) is readily

computed once an expression for $E_{\mathrm{xc}}^{\mathrm{ROPM}}$ in terms of single-particle spinors is given. The remaining functional derivative is calculated by using standard first-order perturbation theory, yielding

$$\frac{\delta\varphi_k(\mathbf{r}')}{\delta A_{S\mu}(\mathbf{r})}=\sum_{\substack{\varepsilon_l\\ l\neq k}}\frac{\varphi_l(\mathbf{r}')}{\varepsilon_k-\varepsilon_l}\overline{\varphi_l}(\mathbf{r})\gamma^\mu\varphi_k(\mathbf{r}). \tag{12}$$

This equation also enables us to give an explicit expression for the response function

$$\chi_S^{\mu\nu}(\mathbf{r},\mathbf{r}'):=\frac{\delta}{\delta A_{S\nu}(\mathbf{r}')}\left(\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}\overline{\varphi_k}(\mathbf{r})\gamma^\mu\varphi_k(\mathbf{r})\right) \tag{13}$$

in terms of the RKS spinors:

$$\chi_S^{\mu\nu}(\mathbf{r}',\mathbf{r})=\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}\sum_{\substack{\varepsilon_l\\ l\neq k}}\frac{\overline{\varphi_k}(\mathbf{r}')\gamma^\mu\varphi_l(\mathbf{r}')\,\overline{\varphi_l}(\mathbf{r})\gamma^\nu\varphi_k(\mathbf{r})}{\varepsilon_k-\varepsilon_l}+\text{c.c.} \tag{14}$$

Finally, putting Eqs. (11), (12), and (14) together leads to the ROPM integral equations for the local xc four-potential $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$:

$$\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}\int d^3r'\left(\overline{\varphi_k}(\mathbf{r}')\gamma^\nu A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}(\mathbf{r}')-\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r}')}\right)G_{Sk}(\mathbf{r}',\mathbf{r})\gamma^0\gamma^\mu\varphi_k(\mathbf{r})+\text{c.c.}=0,$$

$$\mu=0,1,2,3 \tag{15}$$

where $G_{Sk}(\mathbf{r}',\mathbf{r})$ is defined as

$$G_{Sk}(\mathbf{r}',\mathbf{r}):=\sum_{\substack{\varepsilon_l\\ l\neq k}}\frac{\varphi_l(\mathbf{r}')\varphi_l^+(\mathbf{r})}{\varepsilon_k-\varepsilon_l}. \tag{16}$$

Now the ROPM scheme is complete: For a given approximation of the xc energy, the ROPM integral equations have to be solved for $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$ simultaneously with the RKS equation (2) until self-consistency is achieved. Note that Eq. (15) determines the xc four-potential $A_{\mathrm{xc}}^\mu(\mathbf{r})$ only up to an arbitrary constant, which can be specified by requiring $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$ to vanish asymptotically (for finite systems).

To conclude this section, we note that exchange and correlation contributions can be treated separately within the ROPM scheme. This is most easily seen by starting out with only the exchange four-potential, defined as $A_x^\mu(\mathbf{r})=\delta E_x/\delta j_\mu(\mathbf{r})$, instead of Eq. (4) and repeating the steps which lead to Eq. (15) and likewise for the correlation potential.

IV. TRANSFORMATION OF THE ROPM INTEGRAL EQUATIONS AND THE RELATIVISTIC KLI APPROXIMATION

In order to use the ROPM equations derived in the preceding section, we have to solve Eq. (15) for the xc four-potential. Unfortunately, there is no known analytic solution for $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$ depending explicitly on the set of single-particle spinors $\{\varphi_i\}$. We therefore have to deal with Eq. (15) numerically, which is a rather demanding task. Thus a simplified scheme for the calculation of $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$ appears highly desirable.

To this end we shall perform a transformation of the ROPM integral equations similar to the one recently introduced by KLI in the nonrelativistic domain [29,31]. This will lead to an alternative but still exact form of the ROPM integral equation which naturally lends itself as a starting point for systematic approximations. We start out by defining

$$\psi_k^+(\mathbf{r}):=\int d^3r'\left(\overline{\varphi_k}(\mathbf{r}')\gamma^\nu A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}(\mathbf{r}')-\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r}')}\right)G_{Sk}(\mathbf{r}',\mathbf{r}), \tag{17}$$

such that the ROPM integral equations can be rewritten as

$$\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}\overline{\psi_k}(\mathbf{r})\gamma^\mu\varphi_k(\mathbf{r})+\text{c.c.}=0, \tag{18}$$

where the adjoint spinor $\overline{\psi_k}(\mathbf{r})$ is defined in the usual way, i.e.,

$$\overline{\psi_k}(\mathbf{r}):=\psi_k^+(\mathbf{r})\gamma^0. \tag{19}$$

Since the RKS spinors $\{\varphi_i\}$ span an orthonormal set, one readily proves the orthogonality relation

$$\int d^3r\,\psi_k^+(\mathbf{r})\varphi_k(\mathbf{r})=0. \tag{20}$$

We now use the fact that $G_{Sk}(\mathbf{r}',\mathbf{r})$ is the Green function of the RKS equation projected onto the subspace orthogonal to $\varphi_k(\mathbf{r})$, i.e., it satisfies the equation

$$G_{Sk}(\mathbf{r}',\mathbf{r})[\hat{h}_D^+(\mathbf{r})-\varepsilon_k]=-[\delta(\mathbf{r}'-\mathbf{r})-\varphi_k(\mathbf{r}')\varphi_k^+(\mathbf{r})]. \tag{21}$$

The operator $\hat{h}_D^+(\mathbf{r})$ denotes the Hermitian conjugate of the RKS Hamiltonian,

$$\hat{h}_D^+(\mathbf{r}):=\gamma^0[ic\boldsymbol{\gamma}\cdot\overrightarrow{\nabla}+c^2+\gamma^\nu A_{S\nu}(\mathbf{r})], \tag{22}$$

acting from the right on the unprimed variable of $G_{Sk}(\mathbf{r}',\mathbf{r})$ (the arrow on top of the gradient indicates the direction in which the derivative has to be taken). Using Eq. (21), we can act with the operator $[\hat{h}_D^+(\mathbf{r})-\varepsilon_k]$ from the right on Eq. (17), leading to

$$\psi_k^+(\mathbf{r})[\hat{h}_D^+(\mathbf{r})-\varepsilon_k]=-\left(\overline{\varphi_k}(\mathbf{r})\gamma_\nu A_{\mathrm{xc}}^\nu(\mathbf{r})-\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r})}\right)+\varphi_k^+(\mathbf{r})(\overline{A}_{\mathrm{xc}k}^{\mathrm{ROPM}}-\overline{u}_{\mathrm{xc}k}),\tag{23}$$

where we have introduced $\overline{A}_{\mathrm{xc}k}^{\mathrm{ROPM}}$ as a shorthand notation for the average value of $\gamma^\nu A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}(\mathbf{r})$ with respect to the kth orbital, i.e.,

$$\overline{A}_{\mathrm{xc}k}^{\mathrm{ROPM}}:=\int d^3r\,\overline{\varphi_k}(\mathbf{r})\gamma^\nu A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}(\mathbf{r})\varphi_k(\mathbf{r})\tag{24}$$

and

$$\overline{u}_{\mathrm{xc}k}:=\int d^3r\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r}')}\varphi_k(\mathbf{r}).\tag{25}$$

The differential equation (23) has the structure of a RKS equation with an additional inhomogeneity term. Together with the boundary condition

$$\psi_k^+(\mathbf{r})\overset{r\to\infty}{\to}0,\tag{26}$$

Eq. (23) uniquely determines $\psi_k^+(\mathbf{r})$. To prove this statement, we assume that there are two independent solutions of Eq. (23), namely, $\psi_{k,1}^+(\mathbf{r})$ and $\psi_{k,2}^+(\mathbf{r})$. Then the difference of these two solutions, $\Psi_k^+(\mathbf{r}):=\psi_{k,1}^+(\mathbf{r})-\psi_{k,2}^+(\mathbf{r})$, satisfies the homogeneous RKS equation

$$\Psi_k^+(\mathbf{r})[\hat{h}_D^+(\mathbf{r})-\varepsilon_k]=0,\tag{27}$$

which has a unique solution

$$\Psi_k^+(\mathbf{r})=\varphi_k^+(\mathbf{r}),\tag{28}$$

if the above boundary condition is fulfilled. However, this solution leads to a contradiction to the orthogonality relation (20) so that $\Psi_k^+(\mathbf{r})$ can only be the trivial solution of Eq. (27),

$$\Psi_k^+(\mathbf{r})\equiv0,\tag{29}$$

which completes the proof.

As an interesting aside, we briefly consider the physical meaning of the quantity $\psi_k^+(\mathbf{r})$. Defining

$$u_{\mathrm{xc}k}^{\alpha\beta}(\mathbf{r}):=\frac{\delta^{\alpha\beta}}{\varphi_{k\alpha}^*(\mathbf{r})}\frac{\delta E_{\mathrm{xc}}}{\delta\varphi_{k\alpha}(\mathbf{r})},\tag{30}$$

with α and β denoting spinor indices running from 1 to 4, we can rewrite Eq. (17) as

$$\psi_k^+(\mathbf{r})=\sum_{\substack{\varepsilon_l\\ l\neq k}}\frac{\varphi_l^+(\mathbf{r})}{\varepsilon_k-\varepsilon_l}\int d^3r'\,\varphi_{k\alpha}^*(\mathbf{r}')[\gamma^0\gamma^\nu A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}(\mathbf{r}')-u_{\mathrm{xc}k}(\mathbf{r})]^{\alpha\beta}\varphi_{l\beta}(\mathbf{r}'),\tag{31}$$

where summation over α and β is implicitly understood. From this equation, it is obvious that $\psi_k^+(\mathbf{r})$ is the usual first-order shift in the wave function caused by a perturbing potential $\delta A_{\mathrm{xc}}=(\gamma^0\gamma^\nu A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}-u_{\mathrm{xc}k})$. This fact also motivates the boundary condition assumed above. In x-only theory, $u_{\mathrm{xc}k}(\mathbf{r})$ is the local, orbital-dependent RHF exchange potential so that $\psi_k^+(\mathbf{r})$ is the first-order shift of the RKS wave function towards the RHF wave function. However, one has to realize that the first-order shift of the orbital-dependent quantity $u_{\mathrm{xc}k}[\{\varphi_i\}]$ has been neglected.

Now we use Eq. (23) to further transform the ROPM equations (18). As a first step, we solve Eq. (23) for $A_S^0(\mathbf{r})\Psi_k^+(\mathbf{r})$, leading to

$$A_S^0(\mathbf{r})\psi_k^+(\mathbf{r})=-\left(\overline{\varphi_k}(\mathbf{r})\gamma^\nu A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}(\mathbf{r})-\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r})}\right)+(\overline{A}_{\mathrm{xc}k}-\overline{u}_{\mathrm{xc}k})\varphi_k^+(\mathbf{r})-\overline{\psi_k}(\mathbf{r})(ic\boldsymbol{\gamma}\cdot\hat{\boldsymbol{\nabla}}+c^2-\boldsymbol{\gamma}\cdot\mathbf{A}_S(\mathbf{r})-\gamma^0\varepsilon_k).\tag{32}$$

We then multiply the ROPM equations (18) by the zeroth component of the effective RKS four-potential, $A_S^0(\mathbf{r})$, yielding

$$\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}A_S^0(\mathbf{r})\overline{\psi_k}(\mathbf{r})\gamma^\mu\varphi_k(\mathbf{r})+\mathrm{c.c.}=0,\tag{33}$$

and employ Eq. (32) to obtain

$$\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}\left(\overline{\varphi_k}(\mathbf{r})\gamma^\nu A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}(\mathbf{r})-\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r})}-(\overline{A}_{\mathrm{xc}k}^{\mathrm{ROPM}}-\overline{u}_{\mathrm{xc}k})\varphi_k^+(\mathbf{r})+\overline{\psi_k}(\mathbf{r})[ic\boldsymbol{\gamma}\cdot\hat{\boldsymbol{\nabla}}+c^2-\boldsymbol{\gamma}\cdot\mathbf{A}_S(\mathbf{r})-\gamma^0\varepsilon_k]\right)\times\gamma^0\gamma^\mu\varphi_k(\mathbf{r})+\mathrm{c.c.}=0.\tag{34}$$

Introducing the 4×4 matrix

$$\mathcal{J}^{\mu\nu}(\mathbf{r}):=\frac{1}{2}\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}\overline{\varphi_k}(\mathbf{r})\gamma^\nu\gamma^0\gamma^\mu\varphi_k(\mathbf{r})+\mathrm{c.c.}\tag{35}$$

and defining

$$a_{\mathrm{xc}k}^\mu(\mathbf{r}):=\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r})}\gamma^0\gamma^\mu\varphi_k(\mathbf{r})-\overline{\psi_k}(\mathbf{r})[ic\boldsymbol{\gamma}\cdot\hat{\boldsymbol{\nabla}}+c^2-\boldsymbol{\gamma}\cdot\mathbf{A}_S(\mathbf{r})-\gamma^0\varepsilon_k]\times\gamma^0\gamma^\mu\varphi_k(\mathbf{r}),\tag{36}$$

we rewrite Eq. (34) as

$$\mathcal{J}^{\mu\nu}(\mathbf{r})A_{\mathrm{xc}\nu}^{\mathrm{ROPM}}(\mathbf{r})=\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}[a_{\mathrm{xc}k}^\mu(\mathbf{r})+j_k^\mu(\mathbf{r})(\overline{A}_{\mathrm{xc}k}^{\mathrm{ROPM}}-\overline{u}_{\mathrm{xc}k})]+\mathrm{c.c.},\tag{37}$$

with $j_k^\mu(\mathbf{r})$ being the four-current with respect to the kth orbital:

$$j_k^\mu(\mathbf{r}) := \overline{\varphi_k}(\mathbf{r})\,\gamma^\mu\varphi_k(\mathbf{r}). \tag{38}$$

In order to solve Eq. (37) for $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$, we first have to investigate whether the 4×4 matrix $\mathcal{J}(\mathbf{r})$, defined by Eq. (35), is nonsingular, i.e., whether the inverse $\mathcal{J}^{-1}(\mathbf{r})$ exists. We therefore calculate the determinant of $\mathcal{J}(\mathbf{r})$, yielding

$$\det[\mathcal{J}(\mathbf{r})] = [j^0(\mathbf{r})]^2 \cdot j_\mu(\mathbf{r}) j^\mu(\mathbf{r}) = n^4(\mathbf{r})\left(1 - \frac{\mathbf{j}^2(\mathbf{r})}{c^2 n^2(\mathbf{r})}\right), \tag{39}$$

where the last equality follows from the decomposition of the four-current into the scalar density and the vector components according to

$$j^\mu(\mathbf{r}) = \left(n(\mathbf{r}), \frac{1}{c}\mathbf{j}(\mathbf{r})\right). \tag{40}$$

Since the current $\mathbf{j}(\mathbf{r})$ divided by the density $n(\mathbf{r})$ is the velocity field of the system, it follows from $v(\mathbf{r}) < c$ that

$$\det[\mathcal{J}(\mathbf{r})] \neq 0 \tag{41}$$

and therefore that the matrix $\mathcal{J}(\mathbf{r})$ is nonsingular.

Solving then Eq. (37) for $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$ yields

$$A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r}) = \frac{1}{2}\mathcal{J}^{-1}_{\mu\nu}(\mathbf{r}) \sum_{-c^2<\varepsilon_k\leq\varepsilon_F} [a^\nu_{\mathrm{xc}k}(\mathbf{r}) + j_k^\nu(\mathbf{r})(\overline{A}_{\mathrm{xc}k}^{\mathrm{ROPM}} - \overline{u}_{\mathrm{xc}k})] + \mathrm{c.c.} \tag{42}$$

We emphasize that Eq. (42) is an *exact* transformation of the ROPM equation (15). In particular, Eq. (42) is still an integral equation. However, its advantage lies in the fact that it naturally lends itself as a starting point for deriving systematic approximations of $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$: We only need approximate $\psi_k^+(\mathbf{r})$ in Eq. (36) by a suitable function of the set of RKS orbitals $\{\varphi_i\}$. The simplest possible approximation is obtained by completely neglecting the terms involving $\psi_k^+(\mathbf{r})$ in Eq. (36). Although this approximation may seem to be rather crude, it was shown to produce highly accurate results in the nonrelativistic case [29,31].

The xc potential $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$ is then approximately determined by the following equation:

$$A_{\mathrm{xc}\mu}^{\mathrm{RKLI}}(\mathbf{r}) = \frac{1}{2}\mathcal{J}^{-1}_{\mu\nu}(\mathbf{r}) \sum_{-c^2<\varepsilon_k\leq\varepsilon_F} \left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r})}\gamma^0\gamma^\nu\varphi_k(\mathbf{r}) + j_k^\nu(\mathbf{r})(\overline{A}_{\mathrm{xc}k}^{\mathrm{RKLI}} - \overline{u}_{\mathrm{xc}k}) \right) + \mathrm{c.c.} \tag{43}$$

This equation establishes the generalization of the nonrelativistic KLI approximation to the realm of relativistic systems.

In contrast to the ROPM equation (15), the relativistic KLI (RKLI) equation, although still being an integral equation, can be solved explicitly in terms of the RKS spinors $\{\varphi_i\}$: Multiplication of Eq. (43) with $j_l^\mu(\mathbf{r})$, summing over all μ, and integrating over space yields

$$\overline{A}_{\mathrm{xc}l} = \overline{A}^S_{\mathrm{xc}l} + \sum_{-c^2<\varepsilon_k\leq\varepsilon_F} M_{lk}\left(\overline{A}_{\mathrm{xc}k}^{\mathrm{RKLI}} - \frac{1}{2}(\overline{u}_{\mathrm{xc}k} - \overline{u}^*_{\mathrm{xc}k})\right), \tag{44}$$

where we have defined

$$\overline{A}^S_{\mathrm{xc}l} := \int d^3r\, j_l^\mu(\mathbf{r})\mathcal{J}^1_{\mu\nu}(\mathbf{r}) \times\frac{1}{2}\sum_{-c^2<\varepsilon_k\leq\varepsilon_F}\left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r})}\gamma^0\gamma^\nu\varphi_k(\mathbf{r}) + \mathrm{c.c.}\right) \tag{45}$$

and

$$M_{lk} := \int d^3r\, j_l^\mu(\mathbf{r})\mathcal{J}^{-1}_{\mu\nu}(\mathbf{r}) j_k^\nu(\mathbf{r}). \tag{46}$$

The unknown coefficients $[\overline{A}_{\mathrm{xc}k}^{\mathrm{RKLI}} - \frac{1}{2}(\overline{u}_{\mathrm{xc}k} - \overline{u}^*_{\mathrm{xc}k})]$ are then determined by the linear equation

$$\sum_{-c^2<\varepsilon_k\leq\varepsilon_F}(\delta_{lk} - M_{lk})\left(\overline{A}_{\mathrm{xc}k}^{\mathrm{RKLI}} - \frac{1}{2}(\overline{u}_{\mathrm{xc}k} - \overline{u}^*_{\mathrm{xc}k})\right) = \left(\overline{A}^S_{\mathrm{xc}l} - \frac{1}{2}(\overline{u}_{\mathrm{xc}l} - \overline{u}^*_{\mathrm{xc}l})\right). \tag{47}$$

Solving this equation and substituting the result into Eq. (43) finally leads to an expression for the xc four-potential $A_{\mathrm{xc}\mu}^{\mathrm{RKLI}}(\mathbf{r})$ that depends explicitly on the set of single-particle spinors $\{\varphi_i\}$. We thus have obtained a method of calculating the xc four-potential $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}(\mathbf{r})$ in an approximate way, which is numerically much less involved compared to the full solution of the ROPM integral equations.

V. ELECTROSTATIC LIMIT

The ROPM and RKLI methods, developed in the preceding sections, can be applied to systems subject to arbitrary static external four-potentials. In particular, the methods allow us to deal with external magnetic fields of arbitrary strength. Yet, in electronic structure calculations of atoms, molecules, and solids, we most commonly encounter situations, where no magnetic fields are present (in a suitable Lorentz frame, typically the rest frame of the nuclei).

Thus in this section we consider four-potentials whose spatial components vanish, i.e., $\mathbf{A}_{\mathrm{ext}}(\mathbf{r}) = 0$. (This also includes a partial fixing of the gauge.) In this situation, a simplified Hohenberg-Kohn-Sham scheme can be developed, stating that the zeroth component $n(\mathbf{r}) = j^0(\mathbf{r})$ of the ground-state current density alone determines the external potential $V_{\mathrm{ext}}[n]$ and the ground-state wave function $\Psi[n]$ uniquely (for a discussion on this so-called ''electrostatic case'' cf. Refs. [21,23]). Consequently, only a scalar effective potential $V_S(\mathbf{r})$ is present in the RKS equation (2).

When orbital-dependent functionals are used for the xc energy in this context, the corresponding scalar xc potential $V_{\mathrm{xc}}(\mathbf{r})$ can be calculated by repeating the steps of Sec. III. One then finds the ROPM integral equation for the ''electrostatic case'':

$$\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}\int d^3r'\left(\varphi_k^+(\mathbf{r}')V_{\mathrm{xc}}^{\mathrm{ROPM}}(\mathbf{r}')-\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r}')}\right)G_{Sk}(\mathbf{r}',\mathbf{r})\varphi_k(\mathbf{r})+\mathrm{c.c.}=0. \tag{48}$$

We mention that the same result is obtained if one demands that $V_S(\mathbf{r})$ be the variationally best local effective potential yielding single-particle spinors minimizing the total-energy functional (5), i.e.,

$$\left.\frac{\delta E_{\mathrm{tot}}^{\mathrm{ROPM}}}{\delta V_S(\mathbf{r})}\right|_{V_S=V_S^{\mathrm{ROPM}}}=0. \tag{49}$$

In fact, using this approach, Shadwick, Talman, and Norman [22] derived the x-only limit of the ROPM integral equation (48).

Compared to the four ROPM integral equations (15), which determine the xc four-potential $A_{\mathrm{xc}\mu}^{\mathrm{ROPM}}$, Eq. (48) is considerably simpler. Still, its numerical solution is a rather demanding task which has been achieved so far only for systems of high symmetry, i.e., spherical atoms [21–24]. Again, an approximate ROPM scheme can be derived: Following the arguments of Sec. IV, the ROPM integral equation (48) can be exactly rewritten as

$$V_{\mathrm{xc}}^{\mathrm{ROPM}}(\mathbf{r})=\frac{1}{2n(\mathbf{r})}\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}n_k(\mathbf{r})[v_{\mathrm{xc}k}+(\overline{V}_{\mathrm{xc}k}^{\mathrm{ROPM}}-\overline{u}_{\mathrm{xc}k})]+\mathrm{c.c.}, \tag{50}$$

where

$$v_{\mathrm{xc}k}(\mathbf{r}):=\frac{1}{n_k(\mathbf{r})}\left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r})}\varphi_k(\mathbf{r})-ic\nabla[\overline{\psi}_k(\mathbf{r})\boldsymbol{\gamma}\varphi_k(\mathbf{r})]\right) \tag{51}$$

and

$$\psi_k^+(\mathbf{r}):=\int d^3r'\left(\varphi_k^+(\mathbf{r}')V_{\mathrm{xc}}^{\mathrm{ROPM}}(\mathbf{r}')-\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r}')}\right)G_{Sk}(\mathbf{r}',\mathbf{r}) \tag{52}$$

similar to Eq. (17). Equation (50) represents the ''electrostatic case'' analog of Eq. (42) and can also be approximated in the same way, namely, by neglecting all terms involving $\psi_k^+(\mathbf{r})$ in Eq. (51).

In the context of the ''electrostatic case'' considered here, some more insight into the nature of this approximation can be gained: It can be interpreted as a ''mean-field''-type approximation in the sense that the average of the neglected terms with respect to the ground-state density vanishes. To demonstrate this, we note that the neglected terms averaged over $n(\mathbf{r})$ are given by

$$\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}ic\int d^3r\nabla[\overline{\psi}_k(\mathbf{r})\boldsymbol{\gamma}\varphi_k(\mathbf{r})]+\mathrm{c.c.} \tag{53}$$

Applying the divergence theorem, this integral can be transformed to a surface integral which vanishes for finite systems if the surface is taken to infinity. Hence, neglecting the terms involving $\psi_k^+(\mathbf{r})$ means replacing them by their average value, which is zero.

The xc potential $V_{\mathrm{xc}}^{\mathrm{ROPM}}(\mathbf{r})$ can therefore approximately be determined by the following equation, leading to the RKLI equation for the ''electrostatic case'':

$$V_{\mathrm{xc}}^{\mathrm{RKLI}}(\mathbf{r})=\frac{1}{2n(\mathbf{r})}\sum_{-c^2<\varepsilon_k\leqslant\varepsilon_F}\left(\frac{\delta E_{\mathrm{xc}}^{\mathrm{ROPM}}}{\delta\varphi_k(\mathbf{r})}+n_k(\mathbf{r})(\overline{V}_{\mathrm{xc}k}^{\mathrm{RKLI}}-\overline{u}_{\mathrm{xc}k})\right)+\mathrm{c.c.} \tag{54}$$

From this form it is obvious that the RKLI potential closely resembles the relativistic Dirac-Slater potential as well as the nonrelativistic KLI potential. Whether the accuracy of the corresponding nonrelativistic scheme is maintained in the relativistic domain will be investigated in the following section.

VI. RESULTS

In this section, we test the accuracy of the approximate ROPM scheme, derived within the framework of the ''electrostatic case'' in the last section, for atomic systems. In order to assess the quality of this approximation, exact results either for the xc energy E_{xc} or for the xc potential $V_{\mathrm{xc}}(\mathbf{r})$ would be useful. However, for systems where relativistic effects become important, e.g., high-Z atoms, exact results are presently not available. Consequently, we have to look for a different standard to compare with.

Such a standard reference is available within the x-only limit of RDFT [21,23,24]. As in the nonrelativistic case, the x-only limit of the xc energy functional is defined by the use of the exact exchange energy functional, i.e., by the relativistic Fock term, Eq. (6), in the case of only longitudinal (Coulomb) interactions. (Since, in the present context, our principal goal is to the test the quality of the RKLI method, we restrict ourselves to this longitudinal case and neglect transverse contributions.) As explained in the preceding section, the exact longitudinal exchange potential $V_{\mathrm{x}}^{\mathrm{L}}(\mathbf{r})$ can then be obtained by solving the full ROPM integral equation (15) with E_{xc} replaced by $E_x^{L,\mathrm{exact}}$. Simultaneous solution of the ROPM integral equation and the RKS equation (2) therefore represents the exact implementation of the longitudinal x-only limit of RDFT. This scheme will serve as a reference standard in the following.

It is first compared — of course — to the RKLI method, which employs the same exact expression (6) for the exchange energy and only approximates the local exchange potential $V_x^L(\mathbf{r})$ by means of Eq. (54). Besides that, we list the results from traditional RKS calculations obtained with the longitudinal x-only RLDA (xRLDA) and two recently introduced relativistic generalized gradient approximation (RGGA) functionals [24]: The first one is based on the Becke88 GGA [42] (RB88), the second one on a GGA functional due to Engel, Chevary, MacDonald, and Vosko [11] (RECMV92).

These various approaches are analyzed for spherical (closed-shell) atoms. To this end, the spin-angular part of the

TABLE I. Longitudinal ground-state energy $-E_{\mathrm{tot}}^{L}$ from various self-consistent x-only and RHF calculations. $\overline{\Delta}$ denotes the mean absolute deviation and $\overline{\delta}$ the average relative deviation (in 0.1 percent) from the exact ROPM values (all energies are in hartree units).

	RHF	ROPM	RKLI	RB88	RECMV92	xRLDA
He	2.862	2.862	2.862	2.864	2.864	2.724
Be	14.576	14.575	14.575	14.569	14.577	14.226
Ne	128.692	128.690	128.690	128.735	128.747	127.628
Mg	199.935	199.932	199.931	199.952	199.970	198.556
Ar	528.684	528.678	528.677	528.666	528.678	526.337
Ca	679.710	679.704	679.702	679.704	679.719	677.047
Zn	1794.613	1794.598	1794.595	1794.892	1794.880	1790.458
Kr	2788.861	2788.848	2788.845	2788.907	2788.876	2783.282
Sr	3178.080	3178.067	3178.063	3178.111	3178.079	3172.071
Pd	5044.400	5044.384	5044.380	5044.494	5044.442	5036.677
Cd	5593.319	5593.299	5593.292	5593.375	5593.319	5585.086
Xe	7446.895	7446.876	7446.869	7446.838	7446.761	7437.076
Ba	8135.644	8135.625	8135.618	8135.612	8135.532	8125.336
Yb	14067.669	14067.621	14067.609	14068.569	14068.452	14054.349
Hg	19648.865	19648.826	19648.815	19649.141	19649.004	19631.622
Rn	23602.005	23601.969	23601.959	23602.038	23601.892	23582.293
Ra	25028.061	25028.027	25028.017	25028.105	25027.962	25007.568
No	36740.682	36740.625	36740.609	36741.900	36741.783	36714.839
$\overline{\Delta}$			0.006	0.189	0.168	8.668
$\overline{\delta}$			0.002	0.103	0.108	6.20

RKS wave function is treated analytically and the remaining radial Dirac equation is solved numerically on a logarithmic mesh [21]. In all our calculations we use finite nuclei modeled by a homogeneously charged sphere with radius

$$R_{\mathrm{nucl}} = 1.0793\, A^{1/3} + 0.735\,87 \ \ \mathrm{fm}, \tag{55}$$

where A is the atomic mass taken from [43]. We mention in passing that employing finite nuclei is not necessary to ensure convergent results as, for example, in the relativistic Thomas-Fermi model. We incorporate finite nuclei because they represent the physically correct approach.

In Table I, we show the longitudinal ground-state energy E_{tot}^{L} obtained from the various self-consistent x-only RDFT approaches and, in addition, from relativistic Hartree-Fock (RHF) calculations. Comparing the first two columns, we recognize that the RHF and the ROPM data are very close. The largest deviation is found for Be with 41 ppm. With increasing atomic number, the inner orbitals, contributing most to the total energy, become more and more localized such that the difference between the nonlocal RHF potential and the local ROPM decreases. In fact, for No, the difference is down to 2 ppm. We emphasize that these differences are due to the different nature of the two approaches. While the RHF method, by construction, yields the variationally best energy, the ROPM scheme additionally constrains the exchange potential to be local. Consequently, we expect the ROPM results to always be somewhat higher, which is confirmed in Table I. In the third column, the total energies obtained from the RKLI approximation are presented. They always lie above the corresponding ROPM values since the same exchange energy functional is employed in both approaches and the variationally best *local* potential $V_{\mathrm{xc}}^{L,\mathrm{ROPM}}(\mathbf{r})$ is approximated by Eq. (43) in the RKLI approach. However, the results are clearly seen to agree very closely: For the mean absolute deviation from the exact ROPM data of the 18 neutral atoms listed in Table I, one obtains only 5 mhartree. Thus the RKLI method impressively improves on the RLDA results, for which we find a mean absolute deviation of 6092 mhartree. The accuracy of the RKLI scheme becomes even more obvious when compared to the RGGAs. Both RGGAs improve significantly over the RLDA method. Still, their deviations from the exact ROPM data are more than one order of magnitude larger compared to the RKLI results.

The trends found in the above discussion are almost identical to the ones found in the nonrelativistic case. In order to analyze the relativistic effects more directly, we additionally consider the relativistic contribution to E_{tot}^{L}, defined by

$$\Delta E_{\mathrm{tot}} := E_{\mathrm{tot}}^{L}[n^{R}] - E_{\mathrm{tot}}^{NR}[n^{NR}]. \tag{56}$$

Via this decomposition, we are able to test the quality of the RKLI scheme independently of the accuracy of its nonrelativistic equivalent. Yet, at first, we want to point out that the relativistic treatment leads to drastic corrections especially for high-Z atoms. For example, Table II shows that the relativistic correction of Hg amounts for about 6.7% of the total energy thus demonstrating the need for a fully relativistic treatment. Furthermore, by comparing the second and third columns of Table II, we realize that the ROPM and the RKLI method yield almost identical results for the relativistic contribution ΔE_{tot}. In other words, almost no additional deviations are introduced by the relativistic treatment of the KLI

TABLE II. Relativistic contribution $-\Delta E_{\rm tot}^L$ from various self-consistent x-only and RHF calculations. $\overline{\Delta}$ denotes the mean absolute deviation and $\overline{\delta}$ the average relative deviation (in 0.1 percent) from the exact ROPM values (all energies are in hartree units).

	RHF	ROPM	RKLI	RB88	RECMV92	xRLDA
He	0.000	0.000	0.000	0.000	0.000	0.000
Be	0.003	0.003	0.003	0.003	0.003	0.002
Ne	0.145	0.145	0.145	0.145	0.145	0.138
Mg	0.320	0.320	0.320	0.321	0.321	0.308
Ar	1.867	1.867	1.867	1.867	1.867	1.821
Ca	2.953	2.953	2.953	2.952	2.953	2.888
Zn	16.771	16.770	16.770	16.779	16.779	16.555
Kr	36.821	36.820	36.820	36.822	36.821	36.432
Sr	46.554	46.553	46.553	46.552	46.551	46.092
Pd	106.527	106.526	106.526	106.526	106.525	105.715
Cd	128.245	128.243	128.243	128.243	128.241	127.323
Xe	214.860	214.858	214.858	214.825	214.822	213.522
Ba	252.223	252.222	252.221	252.176	252.173	250.725
Yb	676.559	676.551	676.549	676.590	676.588	673.785
Hg	1240.521	1240.513	1240.511	1240.543	1240.538	1236.349
Rn	1736.153	1736.144	1736.142	1736.151	1736.151	1730.890
Ra	1934.777	1934.770	1934.768	1934.781	1934.783	1929.116
No	3953.172	3953.155	3953.151	3953.979	3954.015	3944.569
$\overline{\Delta}$			0.001	0.056	0.058	1.788
$\overline{\delta}$			0.009	1.14	1.35	33.7

scheme. Considering now the relativistic corrections calculated with the conventional RDFT methods, the conclusions drawn in the discussion of $E_{\rm tot}^L$ can be repeated: Compared to the RKLI method, the RGGA results are worse by more than one order of magnitude whereas the RLDA is the by far least accurate approximation.

These trends also remain valid when other quantities of interest are considered. For example, in Tables III and IV we have listed the relativistic contributions to the longitudinal exchange energy, defined analogously to Eq. (56). Again, the RKLI method almost exactly reproduces the ROPM results. It is worthwhile noting that the exchange energy E_x^L is influenced quite substantially by relativistic effects, too. Taking again Hg as an example, we realize that the 5.8% contribution to E_x^L is of the same order as for the total energy. Furthermore, even for lighter atoms such as Mg, the relativistic corrections to E_x^L are comparable or even larger than the differences between the currently best nonrelativistic exchange functionals. As a consequence, a relativistic treatment is indispensable for the ultimate comparison with experiments [21]. Next, we turn our attention to the calculation of ΔE_x from the RGGA functionals listed in the third and fourth columns of Table III. With the exception of No, the results are also in excellent agreement with the exact ones. However, when we turn our attention to other systems like some ions of the neon-isoelectronic series shown in Table IV, we recognize that the RGGAs cannot reproduce the exact results to the same level of accuracy as obtained for the neutral atoms above [24]. This can be explained by the fact that the RGGAs are optimized for the neutral atoms. In contrast, the agreement of the RKLI results with the exact ones for these ions is as good as for the neutral atoms.

TABLE III. Relativistic contribution $-\Delta E_x$ to the exchange energy from various self-consistent x-only calculations. $\overline{\Delta}$ denotes the mean absolute deviation and $\overline{\delta}$ the average relative deviation (in percent) from the exact ROPM values (all energies are in hartree units).

	ROPM	RKLI	RB88	RECMV92	xRLDA
He	0.000	0.000	0.000	0.000	0.000
Be	0.001	0.001	0.001	0.001	0.000
Ne	0.015	0.015	0.015	0.015	0.007
Mg	0.029	0.029	0.029	0.029	0.015
Ar	0.118	0.118	0.117	0.118	0.069
Ca	0.172	0.172	0.171	0.171	0.104
Zn	0.627	0.626	0.632	0.632	0.402
Kr	1.215	1.214	1.212	1.211	0.814
Sr	1.478	1.477	1.473	1.472	1.005
Pd	2.785	2.787	2.782	2.780	1.958
Cd	3.264	3.264	3.255	3.252	2.322
Xe	5.021	5.020	4.977	4.974	3.657
Ba	5.739	5.736	5.684	5.680	4.215
Yb	12.043	12.024	12.027	12.024	9.194
Hg	19.963	19.956	19.965	19.957	15.734
Rn	26.637	26.620	26.612	26.610	21.307
Ra	29.241	29.218	29.225	29.224	23.513
No	52.403	52.402	53.168	53.205	43.683
$\overline{\Delta}$		0.004	0.053	0.056	1.819
$\overline{\delta}$		0.079	1.03	0.857	35.9

TABLE IV. Relativistic contribution $-\Delta E_x$ to the exchange energy from various self-consistent x-only calculations for some ions of the neon-isoelectronic series. $\overline{\Delta}$ denotes the mean absolute deviation and $\overline{\delta}$ the average relative deviation (in percent) from the exact ROPM values (all energies are in hartree units).

	ROPM	RKLI	RB88	RECMV92	xRLDA
Ca^{10+}	0.159	0.160	0.158	0.158	0.093
Zr^{30+}	1.528	1.528	1.507	1.509	0.983
Nd^{50+}	5.780	5.783	5.667	5.675	3.970
Hg^{70+}	15.599	15.606	15.293	15.325	11.365
Fm^{90+}	36.475	36.494	36.258	36.366	28.173
$\overline{\Delta}$		0.006	0.132	0.102	2.992
$\overline{\delta}$		0.041	1.34	1.17	31.8

To further proceed with our investigation, we next raise the question of how well local properties such as the exchange potential $V_x^L(r)$ are reproduced within the different RDFT methods. In Fig. 1, the exchange potential is plotted for the case of Hg. As expected, the RKLI result follows the exact curve most closely. Yet, the pronounced shell structure apparent in the ROPM curve is not fully reproduced, although clearly visible (cf. the more detailed plot in Fig. 2), in the RKLI approximation. However, it again improves significantly over the conventional RDFT results, where the intershell peaks are strongly smeared out or even absent. In Fig. 3, the asymptotic region, which is of particular importance for excitation properties, is plotted in greater detail. There we recover the known deficiencies of the conventional RDFT functionals: The RLDA as well as both RGGAs fall off much too rapidly. In contrast, the RKLI and ROPM curves become indistinguishable in the asymptotic region, both decaying as $1/r$ as $r\to\infty$ and thus reflecting the proper cancellation of self-interaction effects. Since all these observations are already known for the corresponding nonrelativistic functionals, we again consider the relativistic contribution separately. This relativistic contribution to the exchange potential, given by

$$\Delta V_x(r) := \frac{V_x^L[n^R](r) - V_x^{NR}[n^{NR}](r)}{V_x^{\mathrm{OPM}}[n^{NR}](r)}, \tag{57}$$

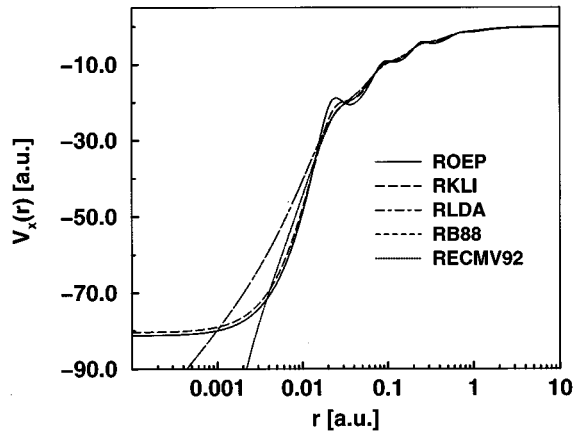

FIG. 1. Longitudinal exchange potential $V_x^L(r)$ for Hg from various self-consistent x-only calculations (in hartree units).

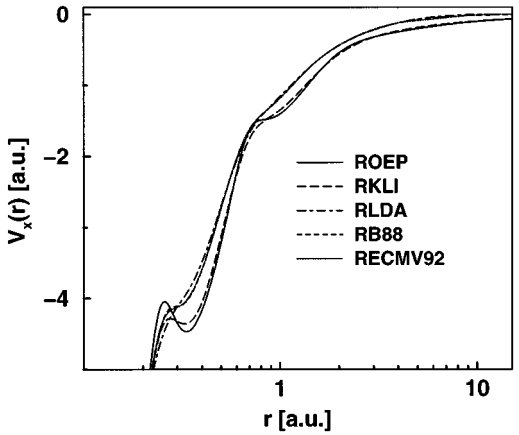

FIG. 2. Longitudinal exchange potential $V_x^L(r)$ for Hg showing the shell structure of Fig. 1 in more detail (in hartree units).

is plotted in Fig. 4. We first observe strong oscillations between 0.1 a.u. and 5 a.u. These oscillations are introduced by the displacement of the density due to relativistic effects and thus represent a direct consequence of the atomic shell structure. As the shell structure of the exchange potential is not fully reproduced within the RKLI approach, the amplitudes of the oscillations are somewhat smaller compared to $\Delta V_x^{\mathrm{OPM}}(r)$. While these deviations are clearly visible, the RKLI curve is still closest to the exact one, especially in the region near the nucleus and in the asymptotic region, where large deviations occur for the conventional RDFT methods.

The properties of the x potential in the large-r asymptotic region also strongly influence the eigenvalue of the highest occupied orbital shown in Table V: Due to the correct asymptotics, the energies calculated within the RKLI scheme are almost identical to the exact ROPM results. On the contrary, the lack of the correct $1/r$ behavior of the RGGAs and the RLDA shows up in rather poorly reproduced eigenvalues of the highest occupied state. Since in the exact nonrelativistic theory, the highest occupied energy level coincides with the ionization potential [44], we also list this quantity, given by $I = E_{\mathrm{tot}}[N-1] - E_{\mathrm{tot}}[N]$, in Table VI. Again, the RKLI and ROPM methods provide almost identical results. In ad-

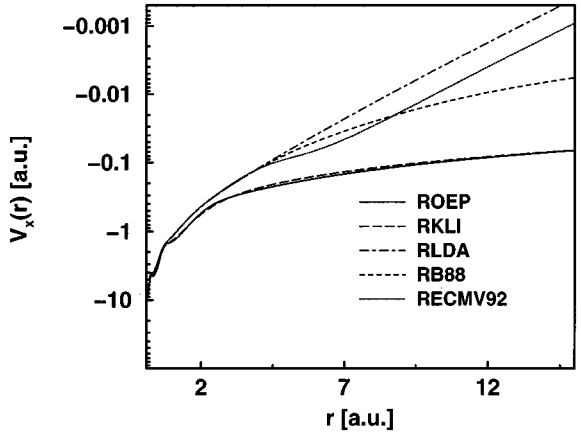

FIG. 3. Asymptotic region of the longitudinal exchange potential of Fig. 1 (in hartree units).

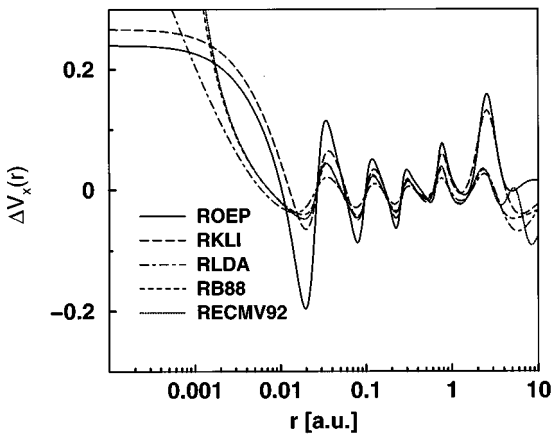

FIG. 4. Relativistic contribution $\Delta V_x(r)$, Eq. (57), for Hg from various self-consistent x-only calculations (in hartree units).

dition, when comparing the ionization potential to the energies of the highest occupied level, we see that the relation $I=\epsilon_N$ — which we of course expect to hold only approximately, since correlation contributions are neglected — is fulfilled within a few percent for the ROPM and RKLI data, whereas the results of the conventional x functional differ to a much larger extent. To conclude, we note that the inclusion of relativistic effects leads to large corrections for heavy atoms even for the outermost orbitals: Taking Hg as an example, we find a 20% shift for the ionization potential.

TABLE V. Eigenenergy $-\epsilon_N$ of the highest occupied orbital from various self-consistent x-only calculations. $\overline{\Delta}$ denotes the mean absolute deviation and $\overline{\delta}$ the average relative deviation (in percent) from the exact ROPM values (all energies are in hartree units).

	ROPM	OPM	RKLI	RB88	RECMV92	xRLDA
Be	0.309	0.309	0.309	0.181	0.182	0.170
Mg	0.253	0.253	0.253	0.149	0.149	0.142
Ca	0.196	0.196	0.196	0.116	0.116	0.112
Zn	0.299	0.293	0.298	0.195	0.194	0.191
Sr	0.181	0.179	0.181	0.108	0.108	0.104
Cd	0.282	0.266	0.282	0.183	0.182	0.181
Ba	0.163	0.158	0.163	0.097	0.097	0.095
Hg	0.329	0.262	0.332	0.223	0.222	0.222
$\overline{\Delta}$			0.001	0.095	0.095	0.099
$\overline{\delta}$			0.156	38.3	38.4	40.0

TABLE VI. Ionization potential calulated from various self-consistent x-only calculations. $\overline{\Delta}$ denotes the mean absolute deviation and $\overline{\delta}$ the average relative deviation (in percent) from the exact ROPM values (all energies are in hartree units).

	ROPM	OPM	RKLI	RB88	RECMV92	xRLDA
Be	0.296	0.295	0.296	0.326	0.327	0.312
Mg	0.243	0.243	0.243	0.269	0.269	0.261
Ca	0.189	0.188	0.189	0.210	0.210	0.205
Zn	0.284	0.278	0.283	0.339	0.338	0.334
Sr	0.175	0.172	0.175	0.195	0.196	0.192
Cd	0.269	0.253	0.268	0.315	0.315	0.314
Ba	0.157	0.152	0.157	0.176	0.176	0.174
Hg	0.313	0.250	0.312	0.364	0.363	0.364
$\overline{\Delta}$			0.000	0.034	0.034	0.029
$\overline{\delta}$			0.130	13.5	13.6	11.6

VII. CONCLUSIONS

In this work, we derived an approximate ROPM scheme generalizing the arguments of Krieger, Li, and Iafrate to the relativistic domain. As for the full ROPM, the advantage of the RKLI method lies in the fact that xc functionals depending explicitly on a set of RKS single-particle spinors can be treated within the framework of RDFT. This, in particular, allows us to employ the exact expression for the exchange energy functional, i.e., the relativistic Fock term in the longitudinal case. Therefore the RKLI approach satisfies a number of important properties, most notably the freedom from self-interactions implying the correct asymptotic decay.

In numerical tests on spherical atoms within the longitudinal x-only limit of RDFT the RKLI method was found to be clearly superior to the known relativistic x-only functionals. The results obtained are seen to be in close agreement with the exact ROPM values, thus reducing the deviation of, for example, the widely used RLDA by more than three orders of magnitude. On the other hand, the numerical effort involved is considerably less compared to the solution of the full ROPM scheme. We therefore expect that the RKLI scheme will be successfully used for larger (nonspherical) systems, e.g., molecules, including also correlation contributions.

ACKNOWLEDGMENTS

Many valuable discussions with K. Capelle, T. Grabo, and M. Lüders are greatly appreciated. One of us (T.K.) acknowledges financial support from the Studienstiftung des deutschen Volkes. This work was supported in part by the Deutsche Forschungsgemeinschaft.

[1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[2] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
[3] R.M. Dreizler and E.K.U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).
[4] R.G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[5] *Density Functional Theory*, Vol. 337 of *NATO Advanced Study Institute, Series B: Physics*, edited by E.K.U. Gross and R.M. Dreizler (Plenum Press, New York, 1995).
[6] R.T. Sharp and G.K. Horton, Phys. Rev. **90**, 317 (1953).

[7] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[8] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **45**, 101 (1992).
[9] Y. Li, J.B. Krieger, and G.J. Iafrate, Chem. Phys. Lett. **191**, 38 (1992).
[10] Y. Li, J.B. Krieger, and G.J. Iafrate, Phys. Rev. A **47**, 165 (1993).
[11] E. Engel, J.A. Chevary, L.D. MacDonald, and S.H. Vosko, Z. Phys. D **23**, 7 (1992).
[12] E. Engel and S.H. Vosko, Phys. Rev. A **47**, 2800 (1993).
[13] E. Engel and S.H. Vosko, Phys. Rev. B **50**, 10 498 (1994).
[14] T. Kotani, Phys. Rev. B **50**, 14 816 (1994); **51**, 13 903 (1995).
[15] T. Kotani, Phys. Rev. Lett. **74**, 2989 (1995).
[16] T. Kotani and H. Akai, Phys. Rev. B **52**, 17 153 (1995); **54**, 16 502 (1996).
[17] D.M. Bylander and L. Kleinman, Phys. Rev. Lett. **74**, 3660 (1995).
[18] D.M. Bylander and L. Kleinman, Phys. Rev. B **52**, 14 566 (1995).
[19] M. Städele, J.A. Majewski, P. Vogl, and A. Görling, in *23rd International Conference on The Physics of Semiconductors*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), p. 613.
[20] A. Görling, Phys. Rev. B **53**, 7024 (1996).
[21] E. Engel, S. Keller, A. Facco Bonetti, H. Müller, and R.M. Dreizler, Phys. Rev. A **52**, 2750 (1995).
[22] B.A. Shadwick, J.D. Talman, and M.R. Norman, Comput. Phys. Commun. **54**, 95 (1989).
[23] E. Engel and R.M. Dreizler, in *Density Functional Theory II*, edited by R.F. Nalewajski (Springer, Berlin, 1996).
[24] E. Engel, S. Keller, and R.M. Dreizler, Phys. Rev. A **53**, 1367 (1996).
[25] E. Engel, S. Keller, and R.M. Dreizler, in *Electronic Density Functional Theory: Recent Progress and New Directions* (Plenum, New York, 1997).
[26] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Lett. A **146**, 256 (1990).
[27] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Lett. A **148**, 470 (1990).
[28] J.B. Krieger, Y. Li, M.R. Norman, and G.J. Iafrate, Phys. Rev. B **44**, 10 437 (1991).
[29] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **46**, 5453 (1992).
[30] J.B. Krieger, Y. Li, and G.J. Iafrate, Int. J. Quantum Chem. **41**, 489 (1992).
[31] J.B. Krieger, Y. Li, and G.J. Iafrate, in *Density Functional Theory*, edited by R.M. Dreizler and E.K.U. Gross (Plenum Press, New York, 1995).
[32] J.B. Krieger, J. Chen, Y. Li, and G.J. Iafrate, Int. J. Quantum Chem. Symp. **29**, 79 (1995).
[33] J.B. Krieger, J. Chen, and G.J. Iafrate, Bull. Am. Phys. Soc. **41**, 748 (1996).
[34] J. Chen, J.B. Krieger, and G.J. Iafrate, Bull. Am. Phys. Soc. **41**, 748 (1996).
[35] J. Chen, J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **54**, 3939 (1996).
[36] J.B. Krieger, Y. Li, Y. Liu, and G.J. Iafrate, Int. J. Quantum Chem. **61**, 273 (1997).
[37] A. Görling and M. Levy, Phys. Rev. A **50**, 196 (1994).
[38] E. Engel, H. Müller, C. Speicher, and R.M. Dreizler, in *Density Functional Theory*, edited by E.K.U. Gross and R.M. Dreizler (Plenum Press, New York, 1995).
[39] A.K. Rajagopal and J. Callaway, Phys. Rev. B **7**, 1912 (1973).
[40] A.K. Rajagopal, J. Phys. C **11**, L943 (1978).
[41] A.H. MacDonald and S.H. Vosko, J. Phys. C **12**, 2977 (1979).
[42] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
[43] K. Hikasa *et al.*, Phys. Rev. D **45**, S1 (1992).
[44] C.O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).