Generalized gradient approximation for the relativistic exchange-only energy functional

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A generalized gradient approximation (GGA) for the exchange energy functional of relativistic many-electron systems, including both a longitudinal and a transverse contribution, is presented. The resulting longitudinal exchange energies for atoms reproduce the corresponding exact values, obtained via the relativistic optimized-potential method, with the same accuracy that has been found for GGAs in the nonrelativistic context. In addition, it is shown that transverse contributions to the self-consistent exchange potential should not be neglected in the case of gradient-corrected functionals.

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In recent years, density-functional theory (DFT) has developed into a rather powerful tool for the description of complex nonrelativistic many-electron systems. In particular, by using generalized gradient approximations (GGAs) for the exchange-correlation (xc) energy functional $E_{\rm xc}[n]$ [1,2] substantial progress has been made towards achieving the accuracy required in quantum chemical applications [3,4]. This type of functional corrects some of the well-known deficiencies of the local-density approximation (LDA), most notably the failure of the LDA to predict the ferromagnetic bcc ground state of metallic iron [5]. While presently available GGAs still do not include important nonlocal contributions to the exact exchange-only (*x*-only) potential [6–8] (which are, e.g., responsible for its asymptotic $-1/r$ behavior in the case of atoms, leading to a somewhat unsatisfactory description of electron affinities and ionization potentials), they are now starting to replace the LDA in applications, in particular, as the additional computational cost of GGAs is rather small.

The forms of all GGAs available to date are based on a combination of both rigorous and semiempirical information on nonrelativistic many-electron systems. Also, their applications are mainly restricted to the nonrelativistic domain of rather light atoms. However, for systems involving atoms with $Z \gtrsim 30$, relativistic effects start to gain importance, not only in the kinetic but also in the xc energy [9,10]. In the context of DFT the nonadditivity of relativistic and xc effects is mainly reflected by a relativistic modification of the functional dependence of $E_{\rm xc}[n]$ on n. This is most easily seen for the relativistic LDA (RLDA), whose *x*-only limit is given by [11–15],

$$E_x^{L/T,\mathrm{RLDA}}[n] = \int d^3r\, e_x^{\mathrm{NRLDA}}(n)\,\Phi_0^{L/T}(\beta), \tag{1}$$

$$e_x^{\mathrm{NRLDA}}(n) = -\frac{3(3\pi^2)^{1/3}e^2}{4\pi} n^{4/3}, \tag{2}$$

$$\Phi_0^L(\beta) = \frac{5}{6} + \frac{1}{3\beta^2} + \frac{2\eta}{3\beta}\,\mathrm{arcsinh}(\beta) - \frac{2\eta^4}{3\beta^4}\ln(\eta) - \frac{1}{2}\left(\frac{\eta}{\beta} - \frac{\mathrm{arcsinh}(\beta)}{\beta^2}\right)^2, \tag{3}$$

$$\Phi_0^T(\beta) = \frac{1}{6} - \frac{1}{3\beta^2} - \frac{2\eta}{3\beta}\,\mathrm{arcsinh}(\beta) + \frac{2\eta^4}{3\beta^4}\ln(\eta) - \left(\frac{\eta}{\beta} - \frac{\mathrm{arcsinh}(\beta)}{\beta^2}\right)^2, \tag{4}$$

where

$$\beta = \frac{(3\pi^2 n)^{1/3}}{mc}; \quad \eta = (1+\beta^2)^{1/2}, \tag{5}$$

and the longitudinal (Coulomb) and transverse (Breit $+\cdots$) parts have been separated, $E_x = E_x^L + E_x^T$ (compare [16–18]). In (1) the relativistic correction (rc) has been written in the form of an rc factor $\Phi_0^{L/T}(\beta)$, which simply multiplies the nonrelativistic LDA [plots of $\Phi_0^{L/T}(\beta)$ can be found in [10,15]]. An analogous functional is obtained for the RLDA correlation energy [10,19], for which, however, the rc factor is only known numerically. Unfortunately, the relativistic corrections to atomic xc energies calculated on the basis of the RLDA are not very accurate: The exact relativistic contribution to the longitudinal *x*-only energy E_x^L, that is, the difference between E_x^L and the nonrelativistic *x*-only energy E_x^{NR},

$$\Delta E_x^L = E_x^L[n^R] - E_x^{\mathrm{NR}}[n^{\mathrm{NR}}], \tag{6}$$

is underestimated by roughly 20–30% [10], while the transverse *x*-only energy E_x^T is overestimated by more than 50% [15,17]. The situation is similar in the case of the correlation energy [10], for which, however, the absolute size of the corrections for atoms is rather small. Consequently, an accurate treatment of the relativistic xc energy requires nonlocal functionals. Focusing on the quantitatively more important *x*-only energy we present a relativistic GGA (RGGA), including both a longitudinal and a transverse component. By application to closed subshell atoms it is shown that this functional yields results comparable in quality to nonrelativistic GGAs. It thus allows an accurate DFT description of ground-state energies and energy differences in the relativistic domain.

Relativistic gradient corrections can be derived in a systematic fashion from the linear response of the relativistic

homogeneous electron gas (RHEG) to a weak perturbing potential [18,20]. For the xc contribution to the induced energy shift one finds

$$\delta E_{\rm xc}^{LR}=\frac{1}{2}\int\frac{d^3q}{(2\pi)^3}\,\delta n(\boldsymbol{q})\,\delta n(-\boldsymbol{q}) \times\left[\frac{1}{\Pi_{00}^{(0)}(q^0=0,\boldsymbol{q})}-\frac{1}{\Pi_{00}(q^0=0,\boldsymbol{q})}\right], \tag{7}$$

where $\Pi_{00}(q^0=0,\boldsymbol{q})$ represents the static irreducible density-density response function of the RHEG ($\Pi_{00}^{(0)}$ is its noninteracting limit) and current contributions have been neglected. The lowest-order gradient correction to the xc energy functional is then obtained by a long wavelength expansion of the response function,

$$\Pi_{00}(q^0=0,\boldsymbol{q})=a(n)+b(n)\boldsymbol{q}^2+\cdots, \tag{8}$$

subtraction of the LDA part of $\delta E_{\rm xc}^{LR}$ and subsequent Fourier transformation. Restriction to the x-only limit, i.e., the first order in e^2, yields

$$\delta E_{\rm xc}^{GE2}[n]=\frac{1}{2}\int d^3r[\nabla n(\boldsymbol{r})]^2\frac{a^{(0)}b^{(1)}-2a^{(1)}b^{(0)}}{(a^{(0)})^3} \tag{9}$$

$$=C_x\int d^3r\; e_x^{\rm NRLDA}(n)\xi\Phi_2(\beta), \tag{10}$$

where $C_x=10/81$. The superscript (k) denotes the order in e^2 of the individual coefficients and the dimensionless characteristic gradient ξ is given by

$$\xi=\left(\frac{\nabla n}{2(3\pi^2 n)^{1/3}n}\right)^2. \tag{11}$$

The argument indicates that a first principles rc factor Φ_2 for the gradient correction could be obtained from the small-q expansion of the first-order response function $\Pi_{00}^{(1)}(0,\boldsymbol{q})$. However, the small-$q$ expansion of $\Pi_{00}^{(1)}(0,\boldsymbol{q})$ is not known to date; only the coefficient $a^{(1)}$ is available via the compressibility sum rule. Given the substantial amount of work that went into the calculation of its nonrelativistic limit [21–25], the evaluation of $b^{(1)}$ does not seem to be an easy task. Moreover, in the nonrelativistic case, it turned out that accurate results for atomic exchange energies were only obtained if the gradient coefficient C_x in (10) was increased to roughly 0.25 [26,27]. Similar semiempirical gradient coefficients are employed in the most widely used GGAs [1,2] (compare [8]). Moreover, GGAs, which may be viewed as an effective partial resummation of the complete gradient expansion,

$$E_x^{\rm NRGGA}[n]=\int d^3r\; e_x^{\rm NRLDA}(n)[1+g(\xi)], \tag{12}$$

$$g(\xi\ll 1)=c_2\xi+c_4\xi^2+\cdots,$$

contain higher-order contributions in ξ whose rc factors are not determined by Eq. (9), but rather by nonlinear response contributions.

In view of the very limited information on relativistic response functions we extend the concept of GGAs to the relativistic domain in a semiempirical way: We use a single rc factor for the complete gradient contribution in the RGGA (split into a longitudinal and a transverse component), which multiplies a given nonrelativistic GGA characterized by $g(\xi)$,

$$E_x^{{\rm RGGA},L/T}[n]=\int d^3r\; e_x^{\rm NRLDA}(n) \times[\Phi_0^{L/T}(\beta)+g(\xi)\Phi_2^{L/T}(\beta)]. \tag{13}$$

For $g(\xi)$ we consider two forms, the widely used GGA by Becke [1],

$$g_{\rm B88}(\xi)=\frac{d\xi}{1+9d\xi^{1/2}{\rm arcsinh}[2(6\pi^2)^{1/3}\xi^{1/2}]/(4\pi)}, \tag{14}$$

($d=0.2743$) and a [2/2]-Padé function (ECMV92) [6],

$$g_{\rm ECMV92}(\xi)=\frac{A_1\xi+A_2\xi^2}{1+B_1\xi+B_2\xi^2}, \tag{15}$$

($A_1=0.3402$, $A_2=5.9955$, $B_1=27.5026$, $B_2=5.7728$) in order to examine the interplay of $g(\xi)$ and the rc factor $\Phi_2^{L/T}(\beta)$. In particular, while the GGAs (14,15) show a similar ξ dependence for intermediate and small ξ, they differ in their large-ξ behavior [6], i.e., in the region close to a (point) nucleus.

For $\Phi_2^{L/T}(\beta)$ we make an ansatz in the form of a [2/2]-Padé function,

$$\Phi_2^{L}(\beta)=\frac{1+a_1^L\beta^2+a_2^L\beta^4}{1+b_1^L\beta^2+b_2^L\beta^4}, \tag{16}$$

$$\Phi_2^{T}(\beta)=\frac{a_1^T\beta^2+a_2^T\beta^4}{1+b_1^T\beta^2+b_2^T\beta^4}, \tag{17}$$

whose parameters are then fitted to exact atomic ΔE_x^L and E_x^T. While the first principles $\Phi_2^{L/T}$ calculated from (9) most likely also depend logarithmically on β [similar to $\Phi_0^{L/T}(\beta)$], the forms (16,17) give the required β^2 proportionality in the weakly relativistic limit ($\beta\ll 1$) and are sufficiently flexible to model the exact $\Phi_2^{L/T}(\beta)$ for intermediate $\beta\approx 1$ (see below). The functional form of the ultrarelativistic limit of the exact $\Phi_2^{L/T}(\beta)$, however, is not known. Moreover, the high-density limit of any $\Phi_2^{L/T}(\beta)$ to be used for atomic systems must be compatible with the large-ξ behavior of $g(\xi)$ in order to yield finite ground-state energies (a discussion of this issue is given in the Appendix). The forms (16,17), which approach a constant for large β, are chosen so that even for point nuclei with Z close to 137 both GGAs give finite results.

The parameters in (16) have been fitted to the exact ΔE_x^L, which are obtained via the optimized-potential method (OPM) [28,10], for 17 closed subshell atoms ranging from He to Ra [30]. To calculate ΔE_x^L in the case of the GGAs we have used exact (R)OPM densities, i.e., for any atom [and given $g(\xi)$] we evaluate (13,16) with the ROPM density and

TABLE I. Parameters for the longitudinal (L) and transverse (T) correction factors (16,17).

	RECMV92		RB88	
	L	T	L	T
a_1	2.212 59	3.487 54	2.208 48	3.486 38
a_2	0.669 152	0.218 599	0.668 684	0.614 753
b_1	1.329 98	1.154 17	1.330 75	1.322 60
b_2	0.794 803	0.015 802	0.795 105	0.101 805

then subtract the corresponding nonrelativistic value calculated by insertion of the nonrelativistic OPM density into (12),

$$\Delta E_x^L(\mathrm{GGA}) = E_x^{\mathrm{RGGA},L}[n^{\mathrm{ROPM}}] - E_x^{\mathrm{NRGGA}}[n^{\mathrm{NROPM}}].$$

In this way a minimization of the percentage deviation of $\Delta E_x^L(\mathrm{GGA})$ from $\Delta E_x^L(\mathrm{OPM})$ (obtained by subtraction of the nonrelativistic OPM exchange energy from $E_x^{L,\mathrm{ROPM}}$) leads to the parameters given in Table I. The corresponding $\Phi_2^L(\beta)$ are shown in Fig. 1. As one might expect from the closeness of the parameters, the two curves for $\Phi_2^L(\beta)$ are indistinguishable. We have also investigated the effect of using self-consistent (R)GGA densities for the optimization procedure. While the precise parameters found in this way differ slightly from the values in Table I, the form of $\Phi_2^L(\beta)$ is essentially unchanged. Moreover, the general form of $\Phi_2^L(\beta)$ is rather similar to that of the exact rc factor for the gradient correction to the kinetic energy [29,18] also displayed in Fig. 1.

In a similar fashion the parameters in (17) have been fitted to $E_x^T(\mathrm{ROPM})$ found by insertion of ROPM spinors into the transverse Fock term [16,30,31] (for the same set of neutral atoms). By minimization of the percentage deviation of $E_x^T(\mathrm{RGGA})$ from $E_x^T(\mathrm{ROPM})$ we have found the parameters (a_i^T, b_i^T), given in Table I. The corresponding $\Phi_2^T(\beta)$ are also plotted in Fig. 1. Again the curves obtained for the two

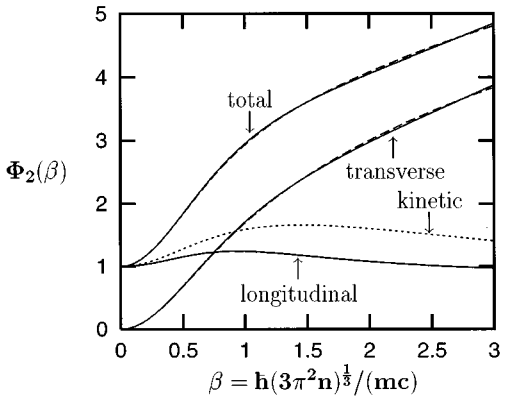

FIG. 1. Relativistic correction factors for the gradient contribution to the exchange-energy density for both ECMV92 (solid line) and B88 (long dashes): Longitudinal contribution (16), transverse contribution (17), and total correction $\Phi_2^L + \Phi_2^T$. Also shown is the rc factor for the gradient correction to the kinetic energy (short dashes).

TABLE II. Nonrelativistic x-only energies ($-E_x^{\mathrm{NR}}$) for closed subshell atoms: OPM results in comparison with the values obtained by insertion of OPM densities into LDA and two GGA functionals (ECMV92 and B88). Also given are the average percentage (%) and absolute (δ) errors (all energies are in hartrees [32]).

Atom	OPM	LDA	ECMV92	B88
He	1.0258	0.8840	1.0258	1.0255
Be	2.6658	2.3124	2.6650	2.6578
Ne	12.105	11.033	12.150	12.138
Mg	15.988	14.612	16.018	16.000
Ar	30.175	27.863	30.166	30.153
Ca	35.199	32.591	35.208	35.192
Zn	69.619	65.645	69.857	69.867
Kr	93.833	88.624	93.843	93.872
Sr	101.926	96.362	101.926	101.956
Pd	139.113	132.169	139.142	139.191
Cd	148.879	141.542	148.879	148.929
Xe	179.062	170.565	178.969	179.041
Ba	189.065	180.240	189.007	189.082
Yb	276.143	265.560	276.880	276.993
Hg	345.240	332.138	345.357	345.486
Rn	387.445	372.974	387.336	387.480
Ra	401.356	386.504	401.255	401.398
%		6.51	0.08	0.10
δ		6.307	0.103	0.102

GGAs are very close to each other. The size of the correction factor is, however, appreciably larger than that of $\Phi_2^L(\beta)$, in accordance with the fact that the error of the RLDA is larger for the transverse energies.

Our results are summarized in Tables II–VI and Figs. 2 and 3. Before turning to an analysis of ΔE_x^L and E_x^T, the *nonrelativistic* exchange energies obtained from the GGAs (14,15) by insertion of OPM densities are shown in Table II and compared with the corresponding OPM and LDA values (in all our calculations extended nuclei were employed [32]). Also given are the average percentage and average absolute errors from the OPM standard (with respect to the 17 atoms listed). While the percentage error is somewhat more sensi-

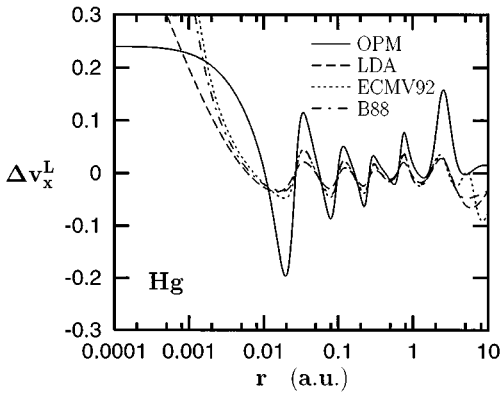

FIG. 2. Percentage relativistic corrections to the longitudinal x-only potential ($[v_x^L - v_x^{\mathrm{NR}}]/v_x^{\mathrm{NROPM}}$) of Hg from self-consistent OPM, LDA, ECMV92, and B88 calculations.

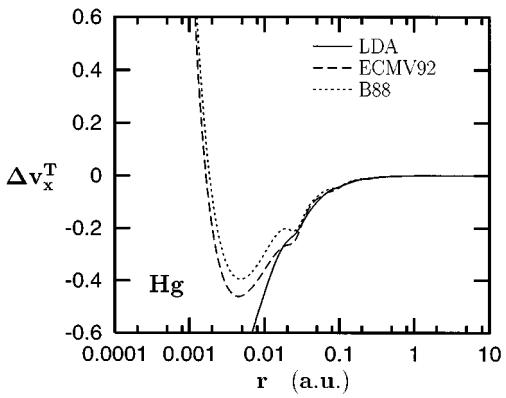

FIG. 3. Percentage transverse corrections ($\Delta v_x^T = v_x^T / v_x^{\mathrm{NROPM}}$) to the x-only potential of Hg from self-consistent relativistic LDA, ECMV92, and B88 calculations.

tive to the accuracy of the E_x^{NRGGA} for light atoms, the absolute error mainly reflects the accuracy for heavier atoms. Table II essentially serves to set a quality standard, which one wants to preserve in the relativistic domain. In particular, Table II demonstrates that the two GGAs yield rather similar results in spite of their different appearance. It should be emphasized that the small difference between the percentage deviations found for the two GGAs is not relevant for practical purposes.

Table III gives ΔE_x^L obtained from the RLDA and the two RGGAs evaluated with (R)OPM densities via (6) in comparison with the ROPM standard. As expected from the agreement between the corresponding Φ_2^L, the two RGGAs yield very similar results. Moreover, the RGGAs impressively improve upon the RLDA: Both average errors are reduced by roughly two orders of magnitude and the average absolute error in $\Delta E_x^L(\mathrm{GGA})$ is one order of magnitude smaller than that in E_x^{NRGGA}. This picture essentially persists if self-consistent (R)GGA-densities are used for the evaluation of $\Delta E_x^L(\mathrm{GGA})$. For example, for RB88 the percentage deviation rises to 0.71%, while the absolute error remains unchanged ($\delta = 9.3$ mhartree). As a consequence the errors of the RGGAs in the total $E_x^{\mathrm{RGGA},L}$ are nearly identical with their nonrelativistic counterparts: For RB88 one finds a percentage deviation of 0.10% and an absolute error of 109 mhartree.

It has been shown [8] that the very accurate reproduction of total atomic exchange energies by nonrelativistic GGAs is to some extent due to the cancellation of much larger local errors, e.g., visible in the exchange potential. The degree to which the accuracy of the RGGAs presented here is based on error cancellation is most directly seen by applying them to two-electron ionic systems: Averaged over the same set of nuclei as used in Table III this leads to deviations of 8.10% and 287 mhartree for ΔE_x^L in the case of B88. While these errors are substantially larger than those found for the neutral atoms, with respect to which Φ_2^L has been optimized, they are still almost one order of magnitude smaller than the corresponding errors of the RLDA (57.57% and 1.281 hartree). We also remark that optimizing Φ_2^L with respect to two-electron ions leads to rc factors that reproduce the ΔE_x^L of these systems much more accurately, but at the price of enhanced errors for neutral atoms.

Table III emphasizes the particular need for rc factors in the case of GGAs: While the Dirac-Fock-Slater approach,

TABLE III. Relativistic corrections to the longitudinal x-only energies ($-\Delta E_x^L$) for closed subshell atoms: ROPM results in comparison with the values obtained by insertion of (R)OPM densities into the relativistic LDA (RLDA), two relativistic GGAs (RECMV92 and RB88), as well as the nonrelativistic LDA (NRLDA) and the corresponding nonrelativistic GGAs (NRECMV92 and NRB88). Also given are the average percentage (%) and absolute (δ) errors (all energies are in hartrees [32]).

	ROPM	RLDA	RECMV92	RB88	NRLDA	NRECMV92	NRB88
He	0.000 063	0.000 026	0.000 064	0.000 064	0.000 058	0.000 071	0.000 071
Be	0.000 72	0.000 31	0.000 71	0.000 70	0.000 66	0.000 79	0.000 79
Ne	0.014 8	0.007 55	0.014 9	0.014 8	0.014 7	0.017 2	0.017 2
Mg	0.028 7	0.015 8	0.028 8	0.028 7	0.028 8	0.033 5	0.033 4
Ar	0.118	0.072	0.118	0.118	0.122	0.139	0.139
Ca	0.172	0.107	0.172	0.171	0.178	0.202	0.202
Zn	0.627	0.409	0.635	0.635	0.673	0.762	0.762
Kr	1.215	0.824	1.215	1.216	1.301	1.462	1.462
Sr	1.478	1.015	1.475	1.476	1.584	1.775	1.775
Pd	2.785	1.971	2.783	2.784	3.029	3.386	3.387
Cd	3.264	2.340	3.260	3.262	3.556	3.966	3.968
Xe	5.021	3.680	4.983	4.986	5.466	6.079	6.081
Ba	5.739	4.237	5.688	5.691	6.249	6.943	6.945
Yb	12.043	9.265	12.072	12.075	13.448	14.980	14.982
Hg	19.963	15.790	19.984	19.989	22.370	24.881	24.888
Rn	26.637	21.371	26.637	26.637	29.848	33.189	33.193
Ra	29.241	23.574	29.247	29.245	32.777	36.445	36.447
%		34.04	0.54	0.50	7.58	19.76	19.69
δ		1.392	0.0096	0.0093	0.723	1.524	1.526

TABLE IV. Single-particle energies ($-\epsilon_{nlj}$) for Hg from relativistic OPM calculations (ROPM) in comparison with self-consistent *x*-only LDA and GGA results without (NRLDA, NRB88), with longitudinal (RLDA, RB88) and with both longitudinal and transverse (RLDA+T, RB88+T) relativistic correction factors (all energies are in hartrees [32]).

Level	ROPM	NRLDA	NRB88	RLDA	RB88	RLDA+T	RB88+T
$1S_{1/2}$	3047.430	3047.517	3050.297	3044.410	3047.643	3027.914	3038.530
$2S_{1/2}$	540.056	539.713	540.180	539.250	539.789	536.824	538.337
$2P_{1/2}$	518.061	518.164	518.467	517.746	518.116	515.615	516.408
$2P_{3/2}$	446.682	446.671	446.875	446.399	446.648	445.025	445.476
$3S_{1/2}$	128.272	128.001	128.135	127.905	128.054	127.397	127.759
$3P_{1/2}$	118.350	118.228	118.312	118.148	118.244	117.736	117.916
$3P_{3/2}$	102.537	102.397	102.456	102.346	102.412	102.084	102.189
$3D_{3/2}$	86.201	86.085	86.120	86.060	86.098	85.934	85.976
$3D_{5/2}$	82.807	82.690	82.722	82.668	82.702	82.559	82.597
$4S_{1/2}$	28.427	28.067	28.130	28.046	28.111	27.931	28.048
$4P_{1/2}$	24.161	23.871	23.911	23.854	23.897	23.770	23.830
$4P_{3/2}$	20.363	20.039	20.081	20.030	20.073	19.980	20.030
$4D_{3/2}$	13.411	13.148	13.169	13.146	13.166	13.133	13.153
$4D_{5/2}$	12.700	12.434	12.455	12.432	12.453	12.423	12.442
$4F_{5/2}$	3.756	3.556	3.559	3.559	3.561	3.571	3.570
$4F_{7/2}$	3.602	3.402	3.405	3.404	3.407	3.417	3.416
$5S_{1/2}$	4.403	4.290	4.292	4.286	4.289	4.267	4.280
$5P_{1/2}$	3.012	2.898	2.898	2.896	2.896	2.885	2.888
$5P_{3/2}$	2.363	2.219	2.225	2.218	2.224	2.213	2.220
$5D_{3/2}$	0.505	0.363	0.366	0.363	0.366	0.364	0.367
$5D_{5/2}$	0.439	0.296	0.299	0.296	0.299	0.297	0.300
$6S_{1/2}$	0.329	0.222	0.223	0.222	0.223	0.220	0.222

i.e., the use of the nonrelativistic LDA functional in relativistic Kohn-Sham calculations, fortuitiously leads to somewhat smaller errors than the RLDA, the insertion of relativistic densities into nonrelativistic GGAs, i.e., a nonlocal extension of the Dirac-Fock-Slater approach, yields values for ΔE_x^L, which, on the average, are 20% too large, so that the absolute errors are even larger than that of the RLDA. Gradient-corrected functionals definitively require relativistic modifications.

We have also examined whether the [2/2]-Padé form (16) is sufficiently flexible to model Φ_2^L by alternatively using a [1/2]- and a [3/3]-Padé ansatz. While, on the basis of B88, the [1/2]-Padé led to an average percentage error of 0.53% and an average absolute error of 15 mhartree, the [3/3]-Padé did not significantly improve upon (16), indicating that the [2/2] form is sufficient for the present purpose.

The percentage rc to the longitudinal *x*-only potential v_x^L,

$$\Delta v_x^L(r) = \frac{v_x^L([n^R];r) - v_x^{\mathrm{NR}}([n^{\mathrm{NR}}];r)}{v_x^{\mathrm{NROPM}}([n^{\mathrm{NROPM}}];r)}, \tag{18}$$

obtained from the RGGAs for Hg is shown together with the corresponding ROPM and RLDA results in Fig. 2. Comparing the RGGAs to the RLDA two features are apparent: Due to the more pronounced shell structure which the GGAs produce (already at the nonrelativistic level [7,8]) the relativistic shifts of the individual shells become more pronounced and follow the ROPM standard more closely. However, in the vicinity of the nucleus (the nuclear radius of Hg is 0.000 13 bohr) the RGGA potential becomes more attractive than the RLDA potential. This region, however, has only little impact even on the $1S_{1/2}$ orbital, whose r-expectation value for Hg is 0.0166 bohr. In any case, as in the nonrelativistic situation [7,8] the GGAs do not improve the potentials as much as the corresponding energies. A quantitative measure of the improvement are the resulting single-particle energies (independent of their auxiliary nature). As can be gleaned from Table IV the eigenvalues obtained from RB88 (similar results are found for RECMV92) agree much better with the ROPM results than those from the RLDA, in particular for the innermost orbitals: For the $1S_{1/2}$-eigenvalue of Hg the RLDA error of 3 hartree is reduced to roughly 200 mhartree, i.e., by one order of magnitude. Furthermore, Table IV again shows that GGAs should not be used in relativistic DFT calculations without rc factors: The deviations of the eigenvalues obtained from GGAs without corrections are as large as those of the RLDA.

Table V lists the transverse energies for neutral atoms calculated from (13,17) by insertion of ROPM densities in comparison with the corresponding RLDA and ROPM data. At first glance, the improvement over the RLDA achieved by the nonlocal functional (13) for the transverse contribution seems to be even more dramatic than that found for the longitudinal component. However, the extremely small deviations of 0.44% and 0.4−0.7 mhartree for neutral atoms are partially due to a fortuitious error cancellation: If one calculates E_x^T of the corresponding two-electron ions using the same Φ_2^T one ends up with an average percentage error of 3.84% and an average absolute error of 151 mhartree (see also the E_x^T for some Hg ions in Table VI). Nevertheless, even these errors are more than one order of magnitude

TABLE V. Transverse x-only energies (E_x^T) for closed subshell atoms: ROPM results in comparison with the values obtained by insertion of ROPM densities into the relativistic LDA (RLDA) and two relativistic GGAs (RECMV92 and RB88). Also given are the average percentage (%) and absolute (δ) errors (all energies are in hartrees [32]).

Atom	ROPM	RLDA	RECMV92	RB88
He	0.000 064	0.000 159	0.000 060	0.000 061
Be	0.000 70	0.001 76	0.000 71	0.000 72
Ne	0.0167	0.0355	0.0166	0.0167
Mg	0.0319	0.0654	0.0319	0.0319
Ar	0.132	0.251	0.132	0.132
Ca	0.191	0.356	0.191	0.191
Zn	0.759	1.328	0.760	0.759
Kr	1.420	2.410	1.421	1.419
Sr	1.711	2.878	1.712	1.710
Pd	3.291	5.374	3.291	3.291
Cd	3.809	6.180	3.809	3.809
Xe	5.712	9.114	5.712	5.713
Ba	6.475	10.282	6.475	6.477
Yb	13.900	21.597	13.895	13.900
Hg	22.169	34.257	22.169	22.169
Rn	28.679	44.382	28.681	28.680
Ra	31.151	48.275	31.149	31.151
%		80.64	0.44	0.44
δ		3.961	0.000 7	0.000 4

smaller than the deviations of the RLDA and thus indicate that the functional (13,17) represents definite progress. As a consequence, the subtle balance between the exact ΔE_x^L and E_x^T [10,18] is well reproduced by the RGGAs, leading to reasonably accurate total corrections $\Delta E_x^L + E_x^T$: For example, for neutral Hg one finds $\Delta E_x^L + E_x^T = 2.180$ hartree using RB88, which may be compared with the exact value of 2.206 hartree and the RLDA result of 18.467 hartree.

The reduced size of the transverse contributions, as compared with the RLDA, also manifests itself in the transverse x-only potential v_x^T, shown in Fig. 3 for Hg. As in the case of v_x^L the (weak) divergence of v_x^T close to the nucleus does not really affect the density. Note, however, that v_x^T becomes appreciable already for the L shell (≈ 0.06 bohr). Without knowledge of the exact multiplicative x-only potential the relevance of this result is difficult to judge. It is, however, supported by the fact that the contribution of the individual orbitals to E_x^T is reproduced rather accurately by the RGGAs, as demonstrated in Table VI by a comparison with ROPM results for some Hg ions. In contrast to the RLDA, which overestimates the exact E_x^T of Hg^{78+} by more than a factor of 2 (i.e., 9 hartree), the error of RB88 is no larger than 6%.

TABLE VI. Transverse x-only energies (E_x^T) for closed subshell Hg ions: ROPM results in comparison with the values obtained by insertion of self-consistent densities into the relativistic LDA (RLDA) and two relativistic GGAs (RECMV92 and RB88) (all energies are in hartrees [32]).

Hg	ROPM	RLDA	RECMV92	RB88
78+	7.578	16.619	6.915	7.112
76+	9.291	20.299	9.018	9.250
70+	16.448	27.780	16.197	16.244
68+	17.057	28.975	16.998	17.049
62+	19.154	31.215	19.172	19.182

Table IV also shows the effect of including v_x^T on the single-particle spectrum of Hg. As expected, the eigenvalue of the $1S_{1/2}$ orbital is substantially reduced (by roughly 9 hartree), but not as much as in the RLDA (17 hartree). The $2P_{3/2}$ eigenvalue also changes by about 1 hartree, and even the $3P_{3/2}$ eigenvalue experiences a 200 mhartree shift. In fact, these corrections are larger than those resulting from the relativistic modification of the longitudinal potential, i.e., the differences between RLDA and Dirac-Fock-Slater eigenvalues. This suggests that the transverse contributions should be treated self-consistently in the case of RGGAs, as, in contrast to the RLDA, for which the error introduced in this way is as large as the transverse correction itself, RGGAs seem to provide a reasonably accurate representation of $E_x^T[n]$.

In summary, our results demonstrate that nonlocal x-only energy functionals like GGAs require a modification in order to preserve their accuracy in the relativistic domain. For GGAs this modification can be accurately represented via a simple rc factor by which their nonrelativistic gradient component $g(\xi)$ is multiplied (together with utilizing the relativistic LDA as basis, of course). The form of this rc factor seems to be rather insensitive to the large-ξ behavior of the gradient correction $g(\xi)$. Moreover, not only the longitudinal but also the transverse contribution should be included in the x-only potential used in relativistic Kohn-Sham calculations.

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APPENDIX: RGGA POTENTIAL IN THE VICINITY OF A POINT NUCLEUS: HIGH-DENSITY LIMIT OF Φ_2

The high-density limit of any semiempirical rc factor for a GGA must be compatible with the large-ξ behavior of $g(\xi)$: In order to obtain a finite ground-state energy E_{tot} the GGA potential must not diverge more strongly than $1/r$ in the vicinity of a point nucleus, as the evaluation of the ground-state energies requires an integration over $n(\boldsymbol{r}) v_x^{\mathrm{RGGA}}(\boldsymbol{r})$ [33,29]. In this respect it is important to notice that resorting to a finite nuclear size, which formally resolves this divergency problem, does not help in practice, as $n(\boldsymbol{r})$ and $v_x^{\mathrm{RGGA}}(\boldsymbol{r})$ remain almost unchanged in the physically relevant regime outside the nucleus and thus spurious contributions to E_{tot} could be produced in this regime if $n(\boldsymbol{r}) v_x^{\mathrm{RGGA}}(\boldsymbol{r})$ becomes too large. It is thus necessary to analyze the consequences of the high-density behavior of Φ_2 for $v_x^{\mathrm{RGGA}}(\boldsymbol{r})$.

Quite generally, both the longitudinal as well as the transverse RGGA potential is given by

$$v_x^{\mathrm{RGGA}}=v_x^{\mathrm{NRLDA}}(n)\Bigg\{\Phi_0(\beta)+\frac{\beta}{4}\frac{d\Phi_0}{d\beta}(\beta)+\frac{\beta}{4}\frac{d\Phi_2}{d\beta}(\beta)\times\Bigg[g(\xi)\quad-2\xi\frac{dg}{d\xi}(\xi)\Bigg]+\Phi_2(\beta)\Bigg[g(\xi)-\frac{3}{2}\eta\frac{dg}{d\xi}(\xi)-\frac{3}{2}\tau\frac{d^2g}{d\xi^2}(\xi)\Bigg]\Bigg\},\tag{A1}$$

where

$$v_x^{\mathrm{NRLDA}}(n)=-\frac{e^2(3\pi^2n)^{1/3}}{\pi},\tag{A2}$$

$$\eta=\frac{\nabla^2 n}{4(3\pi^2n)^{2/3}n},\tag{A3}$$

$$\tau=\frac{\nabla n\cdot\nabla\xi}{4(3\pi^2n)^{2/3}n}.\tag{A4}$$

Considering a point nucleus and assuming the density to behave as

$$n(r)\sim n_0 r^{-3\alpha}$$

in its vicinity ($0<\alpha<2/3$), one finds in leading order,

$$\xi(r)\sim\frac{9\alpha^2}{4(3\pi^2n_0)^{2/3}}r^{2(\alpha-1)},$$

$$\eta(r)\sim\frac{3\alpha(3\alpha-1)}{4(3\pi^2n_0)^{2/3}}r^{2(\alpha-1)}\sim\frac{3\alpha-1}{3\alpha}\xi(r),$$

$$\tau(r)\sim\frac{27\alpha^3(1-\alpha)}{8(3\pi^2n_0)^{4/3}}r^{4(\alpha-1)}\sim 2\frac{1-\alpha}{3\alpha}\xi(r)^2,$$

so that

$$\frac{v_x^{\mathrm{RGGA}}(r)}{v_x^{\mathrm{NRLDA}}(r)}\sim\Phi_0+\frac{\beta}{4}\frac{d\Phi_0}{d\beta}+\frac{\beta}{4}\frac{d\Phi_2}{d\beta}\Bigg[g-2\xi\frac{dg}{d\xi}\Bigg]+\Phi_2\Bigg[g-\frac{3\alpha-1}{2\alpha}\xi\frac{dg}{d\xi}-\frac{1-\alpha}{\alpha}\xi^2\frac{d^2g}{d\xi^2}\Bigg].$$

Inserting the large-ξ behavior of the two GGAs (14,15),

$$g_{\mathrm{B88}}\sim\frac{4\pi\xi^{1/2}}{9\ln[\xi^{1/2}]},$$

$$\frac{dg_{\mathrm{B88}}}{d\xi}\sim\frac{2\pi}{9\xi^{1/2}\ln[\xi^{1/2}]},$$

$$\frac{d^2g_{\mathrm{B88}}}{d\xi^2}\sim-\frac{\pi}{9\xi^{3/2}\ln[\xi^{1/2}]},$$

$$g_{\mathrm{ECMV92}}\sim\frac{A_2}{B_2},$$

$$\frac{dg_{\mathrm{ECMV92}}}{d\xi}\sim\frac{B_1A_2-A_1B_2}{B_2^2\xi^2},$$

$$\frac{d^2g_{\mathrm{ECMV92}}}{d\xi^2}\sim-2\frac{B_1A_2-A_1B_2}{B_2^2\xi^3},$$

one obtains

$$v_x^{\mathrm{RB88}}(r)\propto r^{-\alpha}\Bigg\{\Phi_0+\frac{\beta}{4}\frac{d\Phi_0}{d\beta}+\Phi_2\frac{\pi}{3(\alpha-1)(3\pi^2n_0)^{1/3}}\frac{r^{\alpha-1}}{\ln(r)}\Bigg\}$$

$$v_x^{\mathrm{RECMV92}}(r)\propto r^{-\alpha}\Bigg\{\Phi_0+\frac{\beta}{4}\frac{d\Phi_0}{d\beta}+\Bigg[\Phi_2+\frac{\beta}{4}\frac{d\Phi_2}{d\beta}\Bigg]\frac{A_2}{B_2}\Bigg\}.$$

Consequently, in the case of B88 the critical energy integrand $n(r)v_x^{\mathrm{RGGA}}(r)$ remains integrable close to the nucleus as long as $\Phi_2(\beta)$ does not diverge, $n(r)v_x^{RB88}(r)\propto\Phi_2(\beta)/[r^{3\alpha+1}\ln(r)]$ (as $\alpha<2/3$). ECMV92, however, even allows a logarithmically divergent $\Phi_2(\beta)$ as $n(r)v_x^{\mathrm{RECMV92}}(r)\propto\Phi_2(\beta)/r^{4\alpha}$.

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