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Relativistic Density Functional Calculations of Atoms with B-Splines Basis Functions

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The relativistic density functional theory *is* applied to calculate the ground state total energies for a series of atoms. A B-splines based self-consistent-field procedure is employed to solve the Dirac equation within the local-density approximation, the local-spin-density approximation and the generalized gradient approximation. Both the Gunnarsson-Lundqvist (GL) and the Ceperley-Alder parametrizations as well as their relativistic corrections are used to produce the exchange-correlation energies. The results are compared with the available experimental and other theoretical results. Among various density functional approaches, we find that the total energies of heavy atoms from Hf (Z=72) to Rn (Z=86) calculated in the relativistic local-spin-density (RLSD) approach with the nonrelativistic GL exchange-correlation potential energy agree with the Dirac-Hartree-Fock results within 4 x 10^{-5} a.u..

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I. Introduction

The Hohenberg-Kohn-Sham [1,2] density functional theory (DFT) provides a simple but reliable method for calculating the ground state electronic structures of many-electron systems such as atoms, molecules, and solids [3]. In the DFT approach, the Schrödinger-like single-electron Kohn-Sham equation is obtained by minimizing the total energy functional with respect to the electron density. The Kohn-Sham equation is then solved in a self-consistent-field (SCF) procedure with the many-body effects represented by a local exchange-correlation potential energy functional. Since the SCF iteration of the DFT is quite efficient and converges rapidly, the DFT can be easily applied to large systems. In a previous work [4], we calculated total energies of atoms from H to Sr with the nonrelativistic DFT. The relativistic corrections such as the kinetic energy (P4), the Darwin term (Dw), and the spin-orbital interaction (LS) were also computed with fist order perturbations. In the case of atomic Ge (Z=32), the combined relativistic correction (P4+Dw+LS) accounts for 1.04% of the nonrelativistic total energy. As the atomic number increases, the relativistic effects become more and more important. Therefore, a fully relativistic DFT approach instead of the perturbation treatments should be considered, especially for the innear shell orbitals. The nonrelativistic Hohenberg-Kohn-Sham formalism [1,2] was generalized to the relativistic density functional theory (RDFT) by Rajagopal [5] in 1978 and by MacDonald and Vosko [6] in 1979, separately. In the RDFT approach, the Schrodinger-like equation is replaced by the Dirac-like equation. The non-relativistic exchange-correlation potential energy functional is then replaced by a relativistic corrected functional proposed by MacDonald and Vosko [6] for the relativistic many-body effects.

In the last few years, Kotochigova and coworkers [7] calculated atomic ground state properties across the Periodic Table by four different codes of Froyen, Hamann, Shirley, and Tupitsyn and Kotochigova in the relativistic local-density approximation (RLDA) with the relativistic corrected [6] exchange-correlation potential energy functional of Vosko, Wilk, and Nusair (VWN) [8]. Tong and Chu [9] performed the RDFT calculations for atoms in the Periodic Table in the optimized effective potential (OEP) and self-interaction correction (SIC) approach with the relativistic VWN [8] functional. In this paper, we present calculations in three different RDFT approaches with B-splines basis functions. The Dirac-like equation is solved within the local-density approximation (LDA) [2], the local-spin-density approximation (LSD) [10,11], and the generalized gradient approximation (GGA) [12] respectively. The LDA is the simplest DFT approach with the exchange-correlation potential energy functional depending on the total electron density only. The LSD takes the spin polarization of the electrons into considerations while the gradients of the electron densities are included in the GGA. Both the relativistically modified [6] Gunnarsson-Lundqvist (GL) [11] and Ceperley-Alder (CA) [13,14] exchange-correlation potential energy functionals of the homogeneous electron gas are used in this work.

B-splines [15] are a set of highly localized piecewise polynomial functions defined on a given knot sequence. Since the B-splines basis is quite flexible and powerful, it has recently been used in various atomic calculations [4,16,17,18]. The relativistic electronic structure computations involving solving the Dirac equation in B-splines basis functions are also demonstrated [19]. In this RDFT calculation, we represent major and minor components of the relativistic radial wave functions by linear combinations of B-splines functions and solve the Dirac equation in this basis directly. The SCF procedure is then iterated till the convergence is acceptable.

In the next section, we summarize the RDFT formalism briefly. In section III, we present the total and the orbital energies of a series of atoms computed with various RDFT approaches. The comparisons of the energies obtained in the nonrelativistic and the relativistic modified exchange-correlation potential are presented. The reduced mass and the finite nuclear size effects are discussed. The validity of taking relativistic effects as first order perturbations is also examined. Conclusions are given in the final section IV.

II. Relativistic density functional formalism

The framework of the nonrelativistic density functional theory (DFT), the local density approximation (LDA), the local spin density approximation (LSD), and the generalized gradient approximation (GGA) can be found in Ref. [1],[2],[10,11], and [12] respectively. The relativistic density functional theory (RDFT) is derived in Ref. [5,6] while a relativistic modification for the nonrelativistic exchange-correlation potential energy functionals is proposed in Ref. [6]. We summarize here the RDFT formalism briefly.

In this work the atomic units (a.u.)$\hbar$ = m = e = 1 and c $=\alpha^{-1}=$ 137.0359895 are used. Under the central field approximation of the RDFT, the nonrelativistic radial wave function is replaced by a four component Dirac spinor

$$\psi(r)=\frac{1}{r}\begin{pmatrix} G(r)\chi_{\kappa m}(\hat{r}) \\ iF(r)\chi_{-\kappa m}(\hat{r}) \end{pmatrix}, \tag{1}$$

where G(r) and $F(r)$ are the major and minor components of the radial Dirac wave functions respectively. $\chi_{\kappa m}(\hat{r})$ is an ls coupled spherical spinor. The nonrelativistic single-electron Kohn-Sham equation is replaced by the Dirac equation

$$\begin{aligned} \frac{dF_i(r)}{dr}-\frac{\kappa}{r}F_i(r) &= \alpha[V(r)-\epsilon_i]G_i(r), \\ \frac{dG_i(r)}{dr}+\frac{\kappa}{r}G_i(r) &= \alpha\left[\frac{2}{\alpha^2}+\epsilon_i-V(r)\right]F_i(r). \end{aligned} \tag{2}$$

Here we have replaced the total relativistic energy E by $\epsilon = E - mc^2$ for comparisons with the nonrelativistic calculations. In the Dirac equation, each electron's spin and orbital angular momentum are coupled in two possible values of the total angular momentum: $j=l+1/2$ and $j=l-1/2$, with different wave functions and energies. This is determined by a nonzero integer quantum number K which indicates whether the spin is antiparallel ($\kappa > 0$) or parallel ($\kappa < 0$) to the total angular momentum in the nonrelativistic limit [20]

$$K=\begin{cases} l, & j=1-\frac{1}{2},\ \text{antiparallel, lower level,} \\ -(l+1), & j=1+\frac{1}{2},\ \text{parallel, higher level.} \end{cases} \tag{3}$$

The total electron density is given by summing over all the occupied orbitals

$$\rho(r)=\sum_i w_i\psi_i^{\dagger}(r)\psi_i(r)=\sum_i w_i[|G_i(r)|^2+|F_i(r)|^2], \tag{4}$$

where w_i denotes the occupation numbers. The single-electron potential energy $\mathbf{V(T)}$ in the Dirac equation (2) includes the nuclear attraction, the electron-electron Coulomb repulsion, and the exchange-correction potential v_{xc} which approximates the many-body effects:

$$V(r)=-\frac{z}{r}+\int\frac{\rho(r')}{|r-r'|}dr'+v_{xc}[\rho(r)]. \tag{5}$$

Here v_{xc} is obtained by taking the functional variation of the exchange-correction energy E_{xc} with respect to the electron density $\rho(r)$

$$v_{xc}[\rho(r)]=\frac{\delta E_{xc}[\rho(r)]}{\delta\rho(r)}, \tag{6}$$

where

$$E_{xc}[\rho(r)]=\int\rho(r)\varepsilon_{xc}[\rho(r)]dr. \tag{7}$$

The nonrelativistic exchange-correlation potential $v_{xc}[\rho(r)]$ and the exchange-correlation energy per electron $\varepsilon_{xc}[\rho(r)]$ of homogeneous electron gas have been investigated in various approaches and parameterized in different forms. In this work, both the Gunnarsson-Lundqvist (GL) [11] and the Ceperley-Alder (CA) [13,14] parameterizations are used for the many-body effects. Furthermore, the generalized gradient approximation (GGA) [12] are also used to account for the nonlocal effects. The exchange-correlation potential energy functionals are then modified for the relativistic effects. According to MacDonald and Vosko's proposal [6], the exchange energy per electron ε_x and the potential energy v_x are multiplied respectively by the density-dependent correction factors f_{ε_x} and f_{v_x}:

$$f_{\varepsilon_x}(r_s) = 1 - \frac{3}{2}\left[\frac{(1+\beta^2)^{1/2}}{\beta} - \frac{\ln[\beta + (1+\beta^2)^{1/2}]}{\beta^2}\right]^2, \tag{8}$$

$$f_{v_x}(r_s) = -\frac{1}{2} + \frac{3}{2}\frac{\ln[\beta + (1+\beta^2)^{1/2}]}{\beta(1+\beta^2)^{1/2}}. \tag{9}$$

Here the dimensionless relativistic expansion parameter $\beta = 1/(71.4 r_s)$ and the radius of unit electron charge $r_s = (3/4\pi\rho)^{1/3}/a_0$ in Bohr radius a_0 are used.

In solving equations (2), the coupled Dirac equations are written in the matrix form as

$$\begin{bmatrix} V(r) & c(\kappa/r - d/dr) \\ c(\kappa/r + d/dr) & V(r) - 2mc^2 \end{bmatrix} \begin{bmatrix} G(r) \\ F(r) \end{bmatrix} = \epsilon \begin{bmatrix} G(r) \\ F(r) \end{bmatrix}. \tag{10}$$

This equation may be cast in a generalized eigenvalue equation by expanding the major $G(r)$ and the minor $F(r)$ components of the radial wave function in linear combinations of B-splines functions [15,19,4] $B_i(r)$ of order k as

$$G(r) = \sum_i g_i B_i(r), \qquad F(r) = \sum_i f_i B_i(r), \tag{11}$$

where g_i and f_i are expansion coefficients. A new electron density $\rho(r)$ can then be constructed by equation (4). As the SCF iteration converges, the total ground state energy can be evaluated according to the following formula

$$E_G = \sum_i w_i \epsilon_i - \frac{1}{2}\int d^3r d^3r' \frac{\rho(\vec{r})\rho(\vec{r'})}{|\vec{r} - \vec{r'}|} + \int d^3r \rho(\vec{r})(\varepsilon_{xc}[\rho(\vec{r})] - v_{xc}[\rho(\vec{r})]). \tag{12}$$

III. Results and discussion

Although the relativistic density functional theory (RDFT) and the relativistic correction of the exchange-correlation potential energy functional have been published [5,6] for quite a while: the RDFT have not been performed extensively [7,9] in atomic systems. In this work, we present the self-consistent-field (SCF) RDFT calculations using B-splines basis for a series of atoms. Both the GL [11] and the CA [13,14] parameterizations for the exchange-correlation potential energy functional are used. The results for the spin independent LDA [2], the spin dependent LSD [11], and also the generalized gradient approximation GGA [12] are presented together for comparisons.

The B-splines basis functions [15] of order k defined on a knot sequence $\{t_i\}, i = 1, 2, \ldots$ are a set of positive piecewise polynomials of degree $k-1$. The ith B-spline: $B_{i,k}$ is generated by the following recursion relation [15]:

$$B_{i,k}(x) = \frac{x - t_i}{t_{i+k-1} - t_i} B_{i,k-1}(x) + \frac{t_{i+k} - x}{t_{i+k} - t_{i+1}} B_{i+1,k-1}(x), \tag{13}$$

with

$$B_{i,1}(x) = \begin{cases} 1, & t_i \le x < t_{i+1} \\ 0, & \text{otherwise.} \end{cases} \tag{14}$$

For expanding the orbital wave functions: the B-splines basis used here are constrained in a typical range from 0 to 20 a_0 (Bohr radius) to cover the atomic region. For low-2 atoms such as Kr ($Z=36$), B-splines of order $k = 7$ defined on exponential-type knot sequences are used. The mlmber n of B-splines basis functions is kept less than 60. For atoms of medium-Z such as Xe ($Z=54$), we use $k = 9$ and $n \approx 70$, while for high-Z atoms such as Hg ($Z=80$), $k = 10$ and $n \le 80$ are used in this work.

III-1. Relativistic exchange-correlation energy

In this work, total energies are calculated with both the nomelativistic and the relativistic exchange-correlation potential energy functionals. As pointed out in Ref. [6] that the correlation energy is quite small, the relativistic correction of the correlation energy is neglected. Only the effects from the nonrelativistic and the relativistic exchange energy are actually compared. Table I compares the calculated total ground state energies of atoms from H to Sr in the relativistic local density approximation (RLDA) with the nonrelativistic GL and CA exchange-correlation potential (NREx) as well as with the relativistic modified functionals (REx). The nonrelativistic results from the LDA(GL) and the LDA(CA)[4] are listed in column 2 and 5, respectively, for comparisons. As can be seen in the table, the relativistic effects decrease the total energies systematically. However, there exist significant discrepancies between the total energies calculated with the NREx and with the REx. The total energies from the NREx are systematically lower than those from the REx. Take Ne for example, the difference between the RLDA total energies calculated with the GL(NREx) and with the GL(REx) is 0.0421 a.u. which accounts for 0.033% of the LDA(GL) total energy. For Kr ($Z=36$) the difference grows to 2.8707 a.u. which amounts to 0.10% of the LDA(GL) total energy. Meanwhile, the discrepancy between total energies of Kr from the RLDA(NREx)and the LDA is 36.9249 a.u. Therefore, the relativistic modification of the exchange potential reduces 7.77% of the total relativistic effects in Kr. Similar trends occur also in the CA case.

In column 3 and column 4 of Table II, we list the orbital energies of Pb ($Z=82$) from the RLDA with both the NREx and the REx potential. As the relativistic corrections are included in the exchange potential, the total energy is increased by 44.3411 a.u., with 42.2280 a.u. (95.23%) from the two $1s$ electrons moving in the most relativistic nuclear region. These results are in complete agreements with those mentioned in Ref. [21]. For

TABLE I. Total energies of atoms from H to Sr ($Z=38$).

atom	LDA^{a} GL	RLDA^{b} GL(NREx)	RLDA^{c} GL(REx)	LDA^{d} CA	RLDA^{e} CA(NREx)	RLDA^{f} CA(REx)
H	-0.4537	-0.4537	-0.4537	-0.4459	-0.4459	-0.4459
He	-2.8601	-2.8603	-2.8601	-2.8343	-2.8344	-2.8342
Li	-7.3704	-7.3712	-7.3705	-7.3341	-7.3349	-7.3341
Be	-14.4966	-14.4994	-14.4974	-14.4462	-14.4490	-14.4470
B	-24.4097	-24.4172	-24.4129	-24.3432	-24.3507	-24.3464
C	-37.5095	-37.5262	-37.5184	-37.4243	-37.4409	-37.4331
N	-54.1287	-54.1609	-54.1479	-54.0225	-54.0546	-54.0417
O	-74.5979	-74.6545	-74.6344	-74.4693	-74.5259	-74.5058
F	-99.2466	-99.3397	-99.3101	-99.0946	-99.1876	-99.1580
Ne	-128.4034	-128.5485	-128.5064	-128.2273	-128.3723	-128.3302
Na	-161.6240	-161.8436	-161.7857	-161.4334	-161.6529	-161.5950
Mg	-199.3402	-199.6614	-199.5839	-199.1327	-199.4538	-199.3763
Al	-241.5332	-241.9888	-241.8875	-241.3090	-241.7645	-241.6632
Si	-288.4346	-289.0646	-288.9350	-288.1920	-288.8218	-288.6922
P	-340.2024	-341.0525	-340.8894	-339.9398	-340.7898	-340.6267
S	-396.9931	-398.1177	-397.9157	-396.7093	-397.8338	-397.6318
Cl	-458.9629	-460.4250	-460.1779	-458.6567	-460.1186	-459.8716
Ar	-526.2672	-528.1390	-527.8405	-525.9378	-527.8094	-527.5109
K	-598.5363	-600.9046	-600.5474	-598.1915	-600.5595	-600.2023
Ca	-676.0950	-679.0560	-678.6326	-675.7329	-678.6936	-678.2702
Sc	-759.0536	-762.7089	-762.2121	-758.6692	-762.3242	-761.8274
Ti	-847.6741	-852.1404	-851.5621	-847.2664	-851.7324	-851.1541
V	-942.0990	-947.5062	-946.8378	-941.6673	-947.0742	-946.4059
Cr	-1042.4768	-1048.9582	-1048.1914	-1042.0176	-1048.4986	-1047.7318
Mn	-1148.9172	-1156.6481	-1155.7717	-1148.4363	-1156.1667	-1155.2904
Fe	-1261.5853	-1270.7266	-1269.7314	-1261.0792	-1270.2201	-1269.2249
Co	-1380.6083	-1391.3473	-1390.2226	-1380.0767	-1390.8152	-1389.6906
Ni	-1506.1223	-1518.6627	-1517.3973	-1505.5650	-1518.1049	-1516.8396
Cu	-1638.3566	-1652.8990	-1651.4824	-1637.7696	-1652.3116	-1650.8951
Zn	-1777.1668	-1793.9914	-1792.4091	-1776.5574	-1793.3815	-1791.7992
Ga	-1922.4595	-1941.8322	-1940.0714	-1921.8301	-1941.2020	-1939.4414
Ge	-2074.4416	-2096.6564	-2094.7034	-2073.7912	-2096.0051	-2094.0522
As	-2233.1912	-2258.5556	-2256.3961	-2232.5190	-2257.8824	-2255.7230
Se	-2398.7902	-2427.6396	-2425.2588	-2398.0954	-2426.9439	-2424.5631
Br	-2571.3225	-2604.0168	-2601.3991	-2570.6046	-2603.2979	-2600.6802
Kr	-2750.8731	-2787.7980	-2784.9273	-2750.1315	-2787.0551	-2784.1846
Rb	-2937.0787	-2978.6595	-2975.5191	-2936.3206	-2977.9000	-2974.7597
Sr	-3130.2127	-3176.8964	-3173.4689	-3129.4364	-3176.1186	-3172.6912

a: LDA(GL) [4].
b: RLDA with NREx (GL).
c: RLDA with REx (GL).
d: LDA(CA) [4].
e: RLDA with NREx (CA).
f: RLDA with REx (CA).

TABLE II. Orbital and total energies of Pb (Z=82).

atom	LDA” GL	RLDA^b GL(NREx)	RLDA^c GL(REx)
1s	-2901.0944	-3228.3375	-3207.2235
2s	-488.8578	-577.0094	-573.8452
$2p_{1/2}$	-470.8924	-554.5548	-551.7272
$2p_{3/2}$		-474.1862	-472.3996
3s	-116.5402	-138.4628	-137.7971
$3p_{1/2}$	-107.9638	-128.2411	-127.6898
$3p_{3/2}$		-110.3138	-109.9713
$3d_{3/2}$	-91.9035	-93.3441	-93.1752
$3d_{5/2}$		-89.5253	-89.3808
4s	-25.7661	-31.2933	-31.1423
$4p_{1/2}$	-22.0033	-26.8587	-26.7452
$4p_{3/2}$		-22.4609	-22.3962
$4d_{3/2}$	-15.0427	-15.1950	-15.1784
$4d_{5/2}$		-14.3740	-14.3621
$4f_{5/2}$	-5.6051	-4.9566	-4.9737
$4f_{7/2}$		-4.7716	-4.7888
5s	-4.2181	-5.2585	-5.2331
$5p_{1/2}$	-2.9528	-3.7370	-3.7219
$5p_{3/2}$		-2.9071	-2.9007
$5d_{3/2}$	-0.9130	-0.8106	-0.8130
$5d_{5/2}$		-0.7152	-0.7179
6s	-0.3652	-0.4310	-0.4293
$6p_{1/2}$	-0.1485	-0.1625	-0.1623
E_G	-19520.8316	-20913.2721	-20868.9310
E_x	-345.4690	-370.2333	-325.2941
E_c	-10.4118	-10.4955	-10.4922

a: LDA(GL).

b: RLDA with NREx (GL).

c: RLDA with REx (GL).

higher orbitals, the differences between orbital energies from the REx and the NREx reduces rapidly as shown in the table. As the RLDA results are compared with the LDA ones, the orbital shrinking due to the relativistic kinematic corrections are strong for the inner electrons. This shrinking increases the shielding of the nuclear charge of the outer electrons. On the other hand, the total exchange energy in the RLDA(NREx) is 7.17% lower than that in the LDA. Meanwhile, the RLDA(REx) total exchange energy is 5.84% higher than the LDA ones. This effective exchange interaction decreasing in the relativistic modification of the exchange potential energy functional results from the retardation of the electron-electron Coulomb interaction and the magnetic interaction between moving electrons as were mentioned in Ref. [6, 21].

III-2. Reduced mass and finite nuclear size effects

The assumption that the nucleus is infinitely heavier than the electron is taken in most calculations including this work. For small atoms the point nuclear approximation is also assumed without observable inaccuracy. However, for heavy atoms, the finite size of nucleus should be considered seriously. In this work we also examine the reduced mass and the finite nuclear size effects. The later effects are performed in the uniformly charged nuclear model where the atomic weight A enters as a parameter related to the radius R of the nucleus by $R = \mathbf{2.2677} \times 10^{-5} A^{1/3}$ in a.u. Table III presents the ground state energies calculated in the RLDA with the relativistic modified GL exchange-correlation potential. The total energies E calculated with neither reduced mass nor finite nuclear size effects, with reduced mass only E_μ, with finite nuclear size only E_ν, and with both effects $E_{\mu\nu}$ are listed in column 2, 3, 4, and 5 respectively. We can see that the reduced mass effect raises the total energy by an amount from 4.41×10^{-4} for H to 6.42×10^{-6} for Rb ($Z=37$). This energy shift decreases to an negligible order for larger systems which is in consistent with the original assumption. On the contrary, the finite nuclear size effect increases from 1.0×10^{-6} of F ($Z=9$) to 9.3×10^{-6} of Sr ($Z=38$).

In Table IV we list the influences of the reduced mass μ and the finite nuclear size effects ν on the orbital energies and also the total energy E_G of Xe ($Z=54$). Since for Xe, the former effect is much smaller than the later effect, most of the $\mu\nu$ corrections come from the finite nuclear size effect ν. We can also see that most of the energy shift comes from the s-orbitals, especially 0.2230 a.u. (77.73%) from $1s$ electrons, and 0.0268 a.u. (9.34%) from 2s electrons. This is because that only the inner $1s$ and 2s orbital electrons could penetrate into the finite nuclear region where the infinite nuclear attraction is reduced. Although these two corrections are only 3.86×10^{-5} of the total energy of -7434.6408 a.u., excluding the finite nuclear size effects for heavy atoms causes numerical instabilities in many species.

111-3. Total energies in DFT and RDFT

In Table V we list in each column the calculated total energies in the nonrelativistic LDA, LSD, and GGA as well as the relativistic RLDA, RLSD, and RGGA approaches respectively. The relativistically modified (REx) GL exchange-correlation potential energy functionals are used for the RLDA, the RLSD, and the RGGA. Another RLDA [7] results with the relativistic corrected (REx) VWN [8] exchange-correlation potential functional are listed in column **5.** The last two columns are the Dirac-Hartree-Fock (DHF) [22], and the available experimental [23] results. It is clearly seen in this table that the nonrelativistic

TABLE III. The reduced mass (μ) and the finite nuclear size (ν) effects on the total energies in the RLDA with the relativistic GL exchange-correlation energy.

atom	$-E^{a}$	$-E_{\mu}^{b}$	$-E_{\nu}^{c}$	$-E_{\mu\nu}^{d}$
H	0.4537	0.4535	0.4537	0.4535
He	2.8601	2.8597	2.8601	2.8597
Li	7.3705	7.3699	7.3705	7.3699
Be	14.4974	14.4965	14.4974	14.4965
B	24.4129	24.4117	24.4129	24.4117
C	37.5184	37.5167	37.5184	37.5167
N	54.1479	54.1458	54.1479	54.1458
O	74.6344	74.6319	74.6344	74.6319
F	99.3101	99.3072	99.3100	99.3072
Ne	128.5064	128.5030	128.5064	128.5029
Na	161.7857	161.7819	161.7857	161.7818
Mg	199.5839	199.5794	199.5838	199.5793
Al	241.8875	241.8826	241.8874	241.8825
Si	288.9350	288.9293	288.9348	288.9292
P	340.8894	340.8834	340.8892	340.8832
S	397.9157	397.9089	397.9154	397.9086
Cl	460.1779	460.1708	460.1775	460.1704
Ar	527.8405	527.8332	527.8399	527.8327
K	600.5474	600.5390	600.5467	600.5383
Ca	678.6326	678.6233	678.6317	678.6224
Sc	762.2121	762.2028	762.2108	762.2016
Ti	851.5621	851.5524	851.5605	851.5508
V	946.8378	946.8276	946.8358	946.8256
Cr	1048.1914	1048.1803	1048.1889	1048.1779
Mn	1155.7717	1155.7602	1155.7687	1155.7572
Fe	1269.7314	1269.7190	1269.7277	1269.7153
Co	1390.2226	1390.2097	1390.2180	1390.2051
Ni	1517.3973	1517.3832	1517.3920	1517.3779
Cu	1651.4824	1651.4682	1651.4758	1651.4615
Zn	1792.4091	1792.3941	1792.4012	1792.3862
Ga	1940.0714	1940.0562	1940.0618	1940.0466
Ge	2094.7034	2094.6877	2094.6920	2094.6762
As	2256.3961	2256.3797	2256.3826	2256.3661
Se	2425.2588	2425.2420	2425.2426	2425.2258
Br	2601.3991	2601.3813	2601.3804	2601.3626
Kr	2784.9273	2784.9091	2784.9052	2784.8870
Rb	2975.5191	2975.5000	2975.4935	2975.4744
Sr	3173.4689	3173.4491	3173.4393	3173.4195

a: Excluding both the reduced mass correction (μ) and the finite nuclear size effect (ν).

b: Including the reduced mass correction (μ) only.

c: Including the finite nuclear size effect (ν) only.

d: Including both the reduced mass correction (μ) and the finite nuclear size effect (ν).

TABLE IV. Orbital energies of Xe ($Z=54$) with (column 3) or without (column 2) both the reduced mass effects (μ) and the finite nuclear size effects (ν).

	RLDA	RLDA,,	RLDA”		
atom	GL(REx)	GL(REx)	VWN(REx)	DHF[b]	Expt.[c]
$1s$	-1254.7340	-1254.6225	-1254.7140	-1277.2588	-1270.107
$2s$	-195.4932	-195.4798	-195.4777	-202.4651	-200.401
$2p_{1/2}$	-183.9125	-183.9122	-183.8969	-189.6795	-187.686
$2p_{3/2}$	-172.0992	-172.0992	-172.0837	-177.7047	-175.893
$3s$	-40.0029	-40.0003	-39.9889	-43.0104	-42.213
$3p_{1/2}$	-35.1467	-35.1467	-35.1326	-37.6599	-36.826
$3p_{3/2}$	-32.9020	-32.9020	-32.8880	-35.3254	-34.566
$3d_{3/2}$	-24.2852	-24.2853	-24.2712	-26.0234	-25.320
$3d_{5/2}$	-23.8084	-23.8084	-23.7943	-25.5372	-24.857
$4s$	-7.2221	-7.2216	-7.2095	-8.4299	-7.835
$4p_{1/2}$	-5.4967	-5.4967	-5.4841	-6.4524	-5.696
$4p_{3/2}$	-5.0445	-5.0446	-5.0320	-5.9828	-5.347
$4d_{3/2}$	-2.2406	-2.2406	-2.2283	-2.7114	-2.554
$4d_{5/2}$	-2.1674	-2.1674	-2.1551	-2.6338	-2.481
$5s$	-0.7417	-0.7416	-0.7313	-1.0101	-0.860
$5p_{1/2}$	-0 3499	-0.3499	-0.3402	-0.4926	-0.494
$5p_{3/2}$	-0 3033	-0.3033	-0.2938	-0.4398	-0.446
E_G	-7434.6408	-7434.3539	-7433.4981	-7446.9002	
E_x	-164.9425	-164.9405			
E_c	-6.3597	-6.3596			

a: RLDA(VWN) [7].
b: Dirac-Hartree-Fock [22].
c: Experiment [24].

TABLE V. Total energies in LDA, LSD, GGA, RLDA, RLSD, RGGA, DHF, and available experiments.

atom	LDA' GL	LSD[b] GL	GGA[c] GL	RLDA[d] VWN(REx)	RLDA[e] GL(REx)	RLSD' GL(REx)	RGGA[g] GL(REx)	DHF[h]	Expt[i]
H	-0.4537	-0.4920	-0.5155	-0.4457	-0.4537	-0.4920	-0.5155		
He	-2.8601	-2.8601	-2.9405	-2 8348	-2.8601	-2 8601	-2.9405	-2.8618	-2.9038
Li	-7.3704	-7.3830	-7.5358	-7.3352	-7.3705	-7.3830	-7.5358	-7.4335	-7.4780
Be	-14.4966	-14.4966	-14.7343	-14.4480	-14.4974	-14.4974	-14.7350	-14.5759	-14 6685
B	-24.4097	-24.4198	-24.7483	-24.3413	-24.4129	-24 4230	-24.7512	-24.5366	-24 6579
C	-37.5095	-37.5555	-37.9783	-37 4342	-37.5184	-37.5184	-37.9419	-37.6574	-37.7572
N	-54.1287	-54.2431	-54 7622	-54.0435	-54.1479	-54.1605	-54.6823	-54.3170	-54 4808
0	-74 5979	-74.6526	-75.2754	-74.5087	-74.6344	-74.6890	-75.3108	-74.8393	-75 1101
F	-99 2466	-99.2612	-99.9884	-99.1622	-99.3101	-99.3246	-100.0504	-99.5023	-99.8053
Ne	-128.4034	-128.4034	129.2359	-128.3364	-128.5064	-128.5064	-129.3372	-128 6919	-129.056
Na	-161.6240	-161.6348	-162.5828	-161.6017	-161 7857	-161 7965	-162.7424	-162.0781	-162 441
Mg	-199.3402	-199.3402	-200.4093	-199.3830	-199.5839	-199.5839	-200.6502	-199.9351	-200 333
Al	-241.5332	-241.5397	-242 7293	-241.6693	-241.8875	-241 8941	-243.0802	-242.3311	-242.752
Si	-288 4346	-288.4617	-289.7731	-288.6969	-288.9350	-288.9350	-290.2396	-289.449s	-289 857
P	-340 2024	-340 2661	-341 7012	-340.6310	-340.8894	-340 8963	-342.3217	-341.4889	-342 025
S	-396.9931	-397 0219	-398 5763	-397.6363	-397.9157	-397 9445	-399.4330	-398.6087	-399 144
Cl	-458 9629	-4.58 9703	-460.6449	-459 a773	-460.1779	-460 la53	-461.8531	-460.9398	-461 514
Ar	-526.2672	-526.2672	-528 0651	-527 5190	-527.8405	-527 a405	-529.6305	-528 6838	-529 303
K	-598.5363	-598 5445	-600.4727	-600 2112	-600 5474	-600 5556	-602 4749	-610.5260	
Ca	-676 0950	-676 0950	-678 1564	-678.2793	-678 6326	-678.6326	-680 6839	-679.7102	
SC	-759 0536	-759 0597	-761 2460	-761 a365	-762.2121	-762 2182	-764.3930	-763 3793	
Ti	-847 6741	-847 7007	-850 0093	-8.51 1625	-851 5621	-851 5886	-853.8844	-852.8410	
V	-942.0990	-942.1628	-944 5918	-946.4126	-946.8378	-946 a449	-949.2607	-948.2066	
Cr	-1042.4768	-1042 6734	-1045 2104	-1047.7383	-1048.1914	-1048.1918	-1050.7254	-1049.6764	
Mn	-1148.9172	-1149.1124	-1151.7773	-1155.2942	-1155.7717	-1155.7795	-1158.4289	-1157 3.519	
Fe	-1261.5853	-1261 7154	-1264.4979	-1269 2291	-1269.7314	-1269 7636	-1272.5275	-1271.4403	
CO	-1380 6083	-1380 6841	-1383 5813	-1389 6958	-1390 2226	-1390 2975	-1393.1747	-1392.0688	
Ni	-1506 1223	-1506.1570	-1509.1670	-1516 8469	-1517.3973	-1517 4317	-1520 4202	-1.519 3440	
CU	-1638 3566	-1638 3653	-1641 4765	-1650 9104	-1651 4824	-1651.4172	-1654.5156	-1653 4616	
Zn	-1777 1668	-1777 1668	-1780.3986	-1791 8146	-1792.4091	-1792 4091	-1795.6165	-1794.6133	
Ga	-1922 4595	-1922 4660	-1925 a201	-1939.4536	-1940 0714	-1940 0780	-1943 4055	-1942.5666	
Ge	-2074.4416	-2074 4667	-2077.9412	-2094 0576	-2094.7034	-2094.7034	-2098.1501	-2097 4667	
As	-2233 1912	-2233 2477	-2236 a420	-2255 7273	-2256.3961	-2256 4022	-2259.9664	-2259 4446	
Se	-2398 7902	-2398 8147	-2402 5293	-2424.5681	-2425.2588	-2425.2832	-2428 9648	-2428.6058	
Br	-2571 3225	-2571 3286	-2575 1600	-2600.6885	-2601.3991	-2601.4052	-2605.2013	-2605.0299	
Kr	-2750.8731	-2750 8731	-2754 a217	-2784 1992	-2784.9273	-2784.9273	-2788.8382	-2788 8615	
Rb	-2937.0787	-2937.0861	-2941 1611	-2974 7745	-2975 5191	-2975 5265	-2979.5612	-2979 8059	
Sr	-3130 2127	-3130 2127	-3134 4167	-3172.7058	-3173 4689	-3173 4689	-3177.6296	-3178 0812	

a LDA(GL) 141
b LSD(GL) [4].
c GGA(GL) in this work
d RLDA(VWN)(REx) [7]
e RLDA(GL)(REx) in this work.
f RLSD(GL)(REx) in this work.
g RGGA(GL)(REx) in this work
h: Dirac-Hartree-Fock [22]
i: Experiment [23]

total energies (column 2, 3, 4) are systematically lowered by relativistic effects (column 6, 7, 8). In the LDA scheme, the relativistic total energy shifts grow from 0.08% for Ne $(Z=10)$ to 1.24% for Kr $(Z=36)$. For the LSD case, the relativistic energy corrections are of the same order as in the LDA. Note that there are two exceptions among these atoms. The RLSD total energies of C $(Z=6)$ and N $(Z=7)$ are -37.5184 and -54.1605 a.u. while the nonrelativistic LSD energies are -37.5555 and -54.2431 a.u. respectively. This phenomenon results from the different configuration and coupling scheme between LSD and RLSD. In nonrelativistic LS-coupling scheme, the $2p$ electrons of C and N are of the same spin orientation. However in relativistic jj-coupling scheme, the spins of the two $2p$ electrons in atomic C cancel with each other in the $2p_{1/2}$ state and the total energy is the same as in RLDA for the equal spin occupations. Meanwhile, for atomic N, there is only one electron in $2p_{3/2}$ state above the full $2p_{1/2}$ subshell which is quite different from the nonrelativistic LS-coupling scheme. Although both the GGA and the RGGA total energies are lower than the experimental results, the GGA and RGGA results are generally more accurate than all of the other DFT and the DHF energies.

Table VI shows the orbital energies of Hg $(Z=80)$ from the LDA, the RLDA, and the RGGA with the relativistic (REx) GL exchange-correlation potential energy functionals for the latter two relativistic approaches. Another RLDA [7] with the REx (VWN) [8] exchange-correlation potential, the DHF [22], and the available experimental [24] results are also listed for comparisons. We do not list the corresponding RLSD states here, since for full shell atoms such as Hg, the results are exactly the same as RLDA levels. Compared with the GL [11] exchange-correlation energy, the VWN [8] fitted CA [13] exchange-correlation energy gives lower energies in $1s, 2s$, and 3s orbitals of the highest electron density region while gives higher levels for other orbitals. Since the GGA includes the gradient of electron density as well as the electron density, the exchange potential is stronger in the inner atomic region which both electron density and its gradient are higher. Since the inner orbitals shrink under stronger exchange potential in GGA, the outer electrons become more loosely bounded for screened nuclear attraction forces. This can be seen as the RGGA(GL) orbitals are compared with the RLDA(GL) states, the inner shell states tend to have lower energies while the outer electrons have higher levels in the RGGA. For s, p waves, the inner $(n \leq 4)$ orbitals are lower while the outer $5s, 5p$ and 6s states are higher in the RGGA. For both $4f$ spin parallel and antiparallel states, the RGGA energies are higher. The only exception is that for d orbitals, these tendencies cancel each other.

111-4. Individual relativistic contribution

In a previous work [4], we calculated the atomic total energies with the DFT approaches and obtained the relativistic kinetic energy correction (P4), the Darwin term (Dw), and the spin-orbit interaction (LS) with first order perturbations [25]. Table VII compares the total energies from the nonrelativistic LDA, the relativistic corrected LDA(rel), the RLDA(NREx), and also the relativistic corrections (P4, Dw, and LS). The differences between LDA(rel) and RLDA energies and the ratios (LDA(rel)-RLDA)/RLDA are listed in the last two columns. For $Z \leq 11$, these two approaches agree with each other to the order of truncation errors. The precisions of the LDA(rel) for atoms from Si $(Z=14)$ to Cr $(Z=24)$ and from Mn $(Z=25)$ to Sr $(Z=38)$ are of order 10^{-5} and 10^{-4} of the RLDA total energies respectively. Because of the growing relativistic effects, these discrepancies between total

TABLE VI. Comparisons of orbital energies of Hg (Z=80) in the nomelativistic LDA(GL), the RLDA(GL), and the RGGA(GL) with the relativistic modified exchange-correlation potential.

atom	LDA GL	RLDA GL(REx)	RLDA” VWN(REx)	RGGA GL(REx)	DHF^b	Expt.^{c}
$1s$	-2755.0391	-3028.0482	-3029.9003	-3028.6355	-3074.2346	-3053.952
$2s$	-461.2931	-536.9224	-537.1867	-536.9937	-550.2514	-545.334
$2p_{1/2}$	-443.8634	-515.7152	-515.7076	-515.7530	-526.8530	-522.160
$2p_{3/2}$		-445.1218	-445.0964	-445.1248	-455.1565	-451.424
$3s$	-108.6113	-127.4805	-127.5304	-127.5428	-133.1131	-130.886
$3p_{1/2}$	-100.3415	-117.8196	-117.8078	-117.8465	-122.6385	-120.483
$3p_{3/2}$		-102.1668	-102.1502	-102.1808	-106.5451	-104.629
$3d_{3/2}$	-84.8591	-86.0173	-86.0010	-85.9856	-89.4368	-87.643
$3d_{5/2}$		-82.6426	-82.6265	-82.6114	-86.0202	-84.335
$4s$	-23.2357	-28.0066	-28.0098	-28.0753	-30.6483	-29.410
$4p_{1/2}$	-19.6490	-23.8456	-23.8329	-23.8858	-26.1239	-24.876
$4p_{3/2}$		-20.0548	-20.0411	-20.1096	-22.1885	-20.984
$4d_{312}$	-13.0319	-13.2074	-13.1939	-13.2199	-14.7967	-13.902
$4d_{5/2}$		-12.4967	-12.4833	-12.5116	-14.0526	-13.222
$4f_{5/2}$	-4.1229	-3.6432	-3.6301	-3.6286	-4 4730	-4.083
$4f_{7/2}$		-3.4891	-3.4760	-3.4749	-4.3118	-3.940
$5s$	-3.4350	-4.3319	-4.3234	-4.3149	-5.1030	-4.924
$5p_{1/2}$	-2.2733	-2.9490	-2.9374	-2.9324	-3.5379	-3.318
$5p_{3/2}$		-2.2768	-2.2651	-2.2741	-2.8419	-2.635
$5d_{3/2}$	-0.4633	-0.4247	-0.4137	-0.4197	-0.6501	-0.613
$5d_{5/2}$		-0.3569	-0.3459	-0.3530	-0.5747	-0.548
$6s$	-0.2125	-0.2691	-0.2609	-0.2658	-0.3280	-0.384
E_G	-18406.0695	-19607.7580	-19610.6858	-19616.3524	-19648.8665	
E_x	-331.9940	-313.2165		-324.6333		
E_c	-10.1518	-10.2199		-7.3958		

a: Ref. [7].

b: Dirac-Hartree-Fock [22].

c: Experiment [24].

energies from the relativistic corrected LDA(rel) and the RLDA grow as Z increases. For Sr (Z=38), the corrections of P4 and Dw are -164.7560 a.u. and 119.8034 a.u. which correspond to 5.26% and 3.83% of the LDA total energy of -3130.2127 a.u. respectively. This also indicates that for larger systems the first order perturbation treatments for the relativistic effects becomes unreliable and the fully relativistic RDFT calculations should be considered.

In Table VIII we list the orbital energy levels and the total energy of Au (Z=79) in d-rich configuration calculated in the LDA and the RLDA. The corresponding P4, Dw, LS corrections are also listed for comparisons. For the most relativistical $1s$ orbital, the perturbatively calculated P4 and Dw corrections are -1273.0229 a.u. and 2037.9492 a.u. which corresponds respectively to 47.44% and 75.94% of the LDA $1s$ orbital energy of -2683.5240 a.u.. This seriously conflicts with the assumption of the first order perturbation theory. For the largest spin-orbit interaction (LS) in $2p_{1/2}$ orbital, the correction -35.77478 a.u. is 8.31% of the orbital energy of -430.7396 a.u.. This also makes perturbation calculation unreliable. Although the total perturbative spin-orbit energy shift is zero in atomic Au of d-rich configuration, the total relativistic corrections of P4 and Dw amount to -985.4747 a.u. which is 5.5% of the LDA total energy of -17862.5632 a.u. Besides, the relativistic corrected total energy of -18848.0379 a.u. is 187.0047 a.u. (0.98%) higher than RLDA total energy of -19035.0426 a.u.. If we compare the relativistic corrected LDA(rel) orbital energies with RLDA states, we find that in LDA(rel) the s-orbital energies are higher and the p, d, and f states are lower than in RLDA while these two trends balance in $p_{1/2}$ levels. This is because that the s-orbitals, which could penetrate into the most relativistical region near the nucleus, do not shrink enough as they should. Furthermore, since s-orbitals are too relaxed; the s electron screening effects are relatively small, and the p, d, and f wave functions become tighter.

111-5. Heavy atoms from Hf to Rn

In Table IX we compare different RDFT total energies with DHF results for heavy atoms from Hf (Z=72) to Rn (Z=86). The relativistic total energies are calculated in the RLDA, the RLSD, and the RGGA approaches with both nonrelativistic (NREx) and relativistic modified (REx) GL exchange-correlation potential functionals. For these atoms, the REx typically raises the total energies by about 0.20% in both the RLDA and the RLSD, and by about 0.22% in the RGGA. Since for these heavy atoms the differences of numbers of electrons in different spin orientations are relatively small, the results from the RLSD which takes spin polarization into consideration are quite similar as from the RLDA. For the closed shell atoms such as Hg (Z=80) and Rn (Z=86), the RLDA and the RLSD total energies are exactly the same. The RGGA results which include the effects of the gradient of electron density are about 0.06% lower than the RLSD energies. As compared with the DHF results, we are surprised to observe that the relativistic total energies obtained in the RLSD approach with the NREx (the 5th column) agree fairly well with the DHF energies (the last column). For example, the RLSD(NREx) total energy of Hf (Z=72) is -15088.2615 a.u. which is 3.67 x 10^{-5} higher than -15088.8152 a.u. of DHF. Moreover, the difference decreases as the atomic number increases. For the largest atom Rn (Z=86) listed in the table, the RLSD(NREx) and DHF total energies are -23601.7650 a.u. and -23061.9706 a.u. respectively. The discrepancy between the RLSD(NREx) and the DHF

TABLE VII. Comparisons of total energies from the LDA(GL), from the RLDA(GL), and also the relativistic corrections (P4, Dw, LS).

atom	LDA^a	P4^b	Dw^c	LS^d	LDA(rel)^e	RLDA^f	ΔE^g	$\times 10^{-5\,h}$
H	**-0.4537**	-0.0000	0.0000	0.00000	-0.4537	-0.4537	0.0000	0.0000
He	-2.8601	-0.0007	0.0006	0.00000	-2.8602	-2.8603	0.0001	3.4961
Li	-7.3704	-0.0041	0.0033	0.00000	-7.3712	-7.3712	0.0000	0.0000
Be	-14.4966	-0.0142	0.0113	0.00000	-14.4995	-14.4994	-0.0001	-0.6897
B	-24.4097	-0.0364	0.0290	-0.00008	-24.4172	-24.4172	0.0000	0.0819
C	-37.5095	-0.0781	0.0619	-0.00044	-37.5261	-37.5262	0.0001	0.1599
N	-54.1287	-0.1484	0.1170	-0.00072	-54.1608	-54.1609	0.0001	0.1477
0	-74.5979	-0.2584	0.2028	-0.00090	-74.6544	-74.6545	0.0001	0.1340
F	-99.2466	-0.4208	0.3287	-0.00078	-99.3395	-99.3397	0.0002	0.2215
Ne	-128.4034	-0.6505	0.5058	0.00000	-128.5481	-128.5485	0.0004	0.3112
Na	-161.6240	-0.9684	0.7495	0.00000	-161.8429	-161.8436	0.0007	0.4325
Mg	-199.3402	-1.3942	1.0742	0.00000	-199.6602	-199.6614	0.0012	0.6010
Al	-241.5332	-1.9475	1.4943	-0.00042	-241.9868	-241.9888	0.0020	0.8182
Si	-288.4346	-2.6526	2.0275	-0.00160	-289.0613	-289.0646	0.0033	1.1416
P	-340.2024	-3.5356	2.6925	-0.00204	-341.0475	-341.0525	0.0050	1.4543
S	-396.9931	-4.6244	3.5094	-0.00210	-398.1102	-398.1177	0.0075	1.8839
Cl	-458.9629	-5.9494	4.4998	-0.00155	-460.4141	-460.4250	0.0109	2.3782
Ar	-526.2672	-7.5428	5.6867	0.00000	-528.1233	-528.1390	0.0157	2.9727
K	-598.5363	-9.4460	7.0999	0.00000	-600.8824	-600.9046	0.0222	3.6944
Ca	-676.0950	-11.6954	8.7650	0.00000	-679.0254	-679.0560	0.0306	4.5063
SC	-759.0536	-14.3150	10.7020	-0.00069	-762.6673	-762.7089	0.0416	5.4556
Ti	-847.6741	-17.3516	12.9432	-0.00210	-852.0846	-852.1404	0.0558	6.5482
V	-942.0990	-20.8483	15.5193	-0.00450	-947.4325	-947.5062	0.0737	7.7783
Cr	-1042.4768	-24.8310	18.4519	-0.00696	-1048.8629	-1048.9582	0.0953	9.0890
Mn	-1148.9172	-29.4022	21.8048	-0.00890	-1156.5235	-1156.6481	0.1246	10.7725
Fe	-1261.5853	-34.5551	25.5823	-0.00912	-1270.5672	-1270.7266	0.1594	12.5424
co	-1380.6083	-40.3591	29.8308	-0.00864	-1391.1452	-1391.3473	0.2021	14.5226
Ni	-1506.1223	-46.8672	34.5879	-0.00716	-1518.4088	-1518.6627	0.2539	16.7213
CU	-1638.3566	-54.0990	39.8730	-0.00404	-1652.5866	-1652.8990	0.3124	18.8977
Zn	-1777.1668	-62.2186	45.7856	0.00000	-1793.5998	-1793.9914	0.3916	21.8284
Ga	-1922.4595	-71.2129	52.3242	-0.00688	-1941.3551	-1941.8322	0.4771	24.5506
Ge	-2074.4416	-81.1601	59.5419	-0.01744	-2096.0772	-2096.6564	0.5792	27.6230
As	-2233.1912	-92.1261	67.4842	-0.01626	-2257.8494	-2258.5556	0.7062	31.2695
Se	-2398.7902	-104.1789	76.1981	-0.01330	-2426.7843	-2427.6396	0.8553	35.2318
Br	-2571.3225	-117.3890	85.7318	-0.00806	-2602.9878	-2604.0168	1.0290	39.5174
Kr	-2750.8731	-131.8292	96.1354	0.00000	-2786.5669	-2787.7980	1.2311	44.1603
Rb	-2937.0787	-147.5940	107.4762	0.00000	-2977.1965	-2978.6595	1.4630	49.1161
Sr	-3130.2127	-164.7560	119.8034	0.00000	-3175.1653	-3176.8964	1.7311	54.4903

a: LDA(GL) [4].
b: Relativistic kinetic energy correction (P4) [4].
c: Darwin term effect (Dw) [4].
d: Spin orbital interaction (LS) [4].
e: LDA with perturbatively calculated relativistic corrections (P4+Dw+LS).
f: RLDA with NREx (GL).
g: LDA(rel)-RLDA.
h: (LDA(rel)-RLDA)/RLDA.

TABLE VIII. Comparisons of orbital energies of Au (Z=79) in d-rich configuration from the LDA(GL), from the RLDA(GL), and also the relativistic corrections (P4, Dw, LS).

atom	LDA^a GL	P4^b	Dw^c	LS^d	LDA(rel)^e	RLDA^f GL(NREx)	DHF^g
1s	-2683.5240	-1273.0229	2037.9492		-1918.5977	-2959.9954	-2986.1299
2s	-447.9027	-181.0917	225.2679		-403.7265	-521.9494	-532.1879
$2p_{1/2}$	-430.7396	-30.5663	-1.9559	-35.77478	-499.0366	-500.8460	-509.2779
$2p_{3/2}$	-430.7396	-30.5663	-1.9559	17.88739	-445.3744	-433.4660	-441.7046
3s	-104.8372	-42.9557	50.3372		-97.4557	-123.1797	-128.0890
$3p_{1/2}$	-96.7197	-9.0363	-0.4300	-7.76790	-113.9539	-113.6277	-117.8478
$3p_{3/2}$	-96.7197	-9.0363	-0.4300	3.88395	-102.3021	-98.7627	-102.7322
$3d_{3/2}$	-81.5246	-2.6716	-0.4851	-1.88154	-86.5628	-82.7780	-85.9572
$3d_{5/2}$	-81.5246	-2.6716	-0.4851	1.25436	-83.4269	-79.5800	-82.7386
4s	-22.0904	-10.8744	12.4938		-20.4710	-26.7178	-29.1397
$4p_{1/2}$	-18.5907	-2.3229	-0.1020	-1.83078	-22.8464	-22.6374	-24.7386
$4p_{3/2}$	-18.5907	-2.3229	-0.1020	0.91539	-20.1002	-19.0634	-21.0681
$4d_{3/2}$	-12.1438	-0.7020	-0.1005	-0.38832	-13.3346	-12.3567	-13.8665
$4d_{5/2}$	-12.1438	-0.7020	-0.1005	0.25888	-12.6874	-11.6909	-13.1725
$4f_{5/2}$	-3.4987	-0.1575	-0.0630	-0.08572	-3.8049	-3.0799	-3.8680
$4f_{7/2}$	-3.4987	-0.1575	-0.0630	0.06429	-3.6549	-2.9396	-3.7207
5s	-3.1248	-2.1434	2.4485		-2.8197	-3.9958	-4.6844
$5p_{1/2}$	-2.0132	-0.4014	-0.0169	-0.30912	-2.7406	-2.6659	-3.1892
$5p_{3/2}$	-2.0132	-0.4014	-0.0169	0.15456	-2.2769	-2.0531	-2.5590
$5d_{3/2}$	-0.3149	-0.0664	-0.0089	-0.03492	-0.4251	-0.3074	-0.4934
$5d_{5/2}$	-0.3149	-0.0664	-0.0089	0.02328	-0.3669	-0.2507	-0.4288
6s	-0.1690	-0.1542	0.0880		-0.2352	-0.2317	-0.2916
E_G	-17862.5632	-3310.8971	2325.4224		-18848.0379	-19035.0426	-19035.5586
E_x	-325.2392					-346.5476	
E_C	-10.0156					-10.0791	

a: LDA(GL) [4].
b: Relativistic kinetic energy correction (P4) [4].
c: Darwin term correction (Dw) [4].
d: Spin-orbit interaction (LS) [4].
e: Relativistic corrected LDA(rel).
f: RLDA with NREx (GL) in this work.
g: Dirac-Hartree-Fock [22].

TABLE IX. Comparisons of relativistic total energies of heavy atoms from Hf (Z=72) to Rn (Z=86) in different RDFT approaches with both the nonrelativistic (NREx) and the relativistic (REx) GL exchange-correlation potential energies.

atom	*	RLDA NREx	RLDA REX	RLSD NREx	RLSD REx	RGGA NREx	RGGA REX	DHF^a
Hf	$5d^{2}_{3/2}6s^{2}$	-15088.2429	-15060.0131	-15088.2615	-15060.0317	-15098.2783	-15067.8936	-15088.8152
Ta	$5d^{3}/26s^{2}$	-15616.0680	-15586.4773	-15616.0728	-15586.4821	-15626 2975	-15594.4406	-1.5616 6609
W	$5d^{4}_{3/2}6s^{2}$	-16155.6341	-16124.6317	-16155.6341	-16124.6317	-16166.0686	-16132.6837	-16156.2463
Re	$5d^{1}_{5/2}6s^{2}$	-16707.0723	-16674.6055	-16707.0771	-16674.6103	-16717.7258	-16682 7552	-16707.6792
OS	$5d^{2}_{5/2}6s^{2}$	-17270 5466	-17236.5617	-17270.5660	-17236.5811	-17281.4343	-17244.8186	-17271.1551
Ir	$5d^{5}/26s^{2}$	-17846.2540	-17810.6948	-17846.2983	-17810.7391	-17857.3928	-17819.0703	-17846.8566
Pt	$5d^{5}/26s^{1}$	-0434 3565	-18397.1679	-18434.3726	-18397.1840	-18445.6879	-18405.5977	-18434.9109
AU	$5d^{6}_{5/2}6s^{1}$	-19035 0 4 2 6	-18996.1624	-19035.0487	-18996.1685	-19046.5981	-19004.6716	-19035 5586
Hg	$5d^{6}_{5/2}6s^{2}$	-19648.3941	-19607.7580	-19648.3941	-19607.7580	-19660.1861	-19616.3524	-19648.8665
Tl	$6s^{2}6p^{1}_{1/2}$	-20274.3495	-20231.8943	-20274.3551	-20231.8999	-20286.4002	-20240.5893	-20274.8261
Pb	$6s^{2}6p^{2}_{1/2}$	-20913.2721	-20868.9310	-20913.2721	-20868.9310	-20925.5743	-20877 7121	-20913.7151
Bi	$6s^{2}6p^{1}_{3/2}$	-21565.2827	-21518.9870	-21565.2876	-21518.9919	-21577.8543	-21527.8645	-21565 6930
PO	$6s^{2}6p^{2}_{3/2}$	-22230 6270	-22182.3050	-22230.6460	-22182.3241	-22243 4820	-22191 2047	-22230.9946
At	$6s^{2}6p^{3}_{3/2}$	-22909 4581	-22859.0362	-22909.4627	-22859.0407	-22922.5732	-22868.0865	-22909.7492
Rn	$6s^{2}6p^{4}_{3/2}$	-23601 7650	-23549 1693	-23601 7650	-23549 1693	-23615.1543	-23558.2966	-23601.9706

* **Valence** shellconfiguration
a Dirac-Elartree-Fock [22]

is only 8.71 x 10^{-6} of the DHF total energy. However, we do not know how to explain this interesting issue yet.

IV. Conclusion

In this paper we present applications of B-splines based relativistic density functional theory (RDFT) calculations for a series of atoms. We calculate orbital and total energies in the RLDA, the RLSD, and the RGGA approaches with both the GL and the CA exchange-correlation potential energy functionals. In all the RDFT calculations, the relativistic effects systematically improve the nonrelativistic results. Meanwhile, the relativistic modified exchange-correlation potential energy functional systematically raises the total energies of all the calculated species. The accuracies of the nonrelativistic results and the validity of taking relativistic effects as first order perturbations are discussed. We are surprised to observe that the relativistic ground state total energies for heavy atoms from Hf (Z=72) to Rn (Z=86) obtained from the RLSD approach with the nonrelativistic GL exchange-correction potential energy functional agree with the Dirac-Hartree-Fock (DHF) [22] results to five digits. We do not know how to explain it yet. A further investigation might solve this issue.

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