

# Exchange-Correlation Functional Comparison of Electronic Energies in Atoms Using a Grid Basis

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**How to cite this paper:** Ryan, A.D., Gama, A., Felerski, F. and Parker, W.D. (2022) Exchange-Correlation Functional Comparison of Electronic Energies in Atoms Using a Grid Basis. *Journal of Applied Mathematics and Physics*, **10**, 3392-3407. <https://doi.org/10.4236/jamp.2022.1011225>

**Received:** October 22, 2022

**Accepted:** November 26, 2022

**Published:** November 29, 2022

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## Abstract

Calculation of total energies of the electronic ground states of atoms forms the basis for the frozen-core pseudopotentials used in atomistic calculations of much larger scale. Reference values for these energies provide a benchmark for the validation of new software to calculate such potentials. In addition, basic atomic-scale electronic properties such as the (first) ionization energy provide a simple check on the approximation used in the calculation method. We present a comparison of the total energies and ionization energies of atoms  $Z = 1 - 92$  calculated in density functional theory with several levels of exchange-correlation functional and the Hartree-Fock method, comparing ionization energies to experiment. We also investigate the role of relativistic treatment on these energies.

## Keywords

Density Functional Theory, Hartree-Fock Theory, Electronic Energies, Exchange-Correlation Potential, Exchange and Correlation Functional, Ionization Energy

## 1. Introduction

Density functional theory (DFT) is a quantum mechanical method widely used in chemistry [1] and materials science [2] to calculate system properties from first principles within its one significant approximation: the exchange-correlation functional. DFT calculations of atomic total electronic energies are important for calibrating advancements in exchange-correlation functionals among codes [3] and producing reliable pseudopotentials [4]. Recent advances in exchange-correlation functionals continue to show reduced error in molecular [5] [6] and solid-state

[6] [7] test sets compared and call for an investigation of the functionals' effect on energies calculated in isolated atoms.

Non-empirical pseudopotentials constructed for use with plane waves in DFT simulations of systems with periodic boundary conditions rely on atomic calculations in which the electrons are represented through Kohn-Sham states constituting the electron density on a radial grid [8]. Existing research has explored the effects of exchange-correlation functional at the local-density [8] and generalized-gradient [9] [10] levels of approximation, including the effects of incorporating spin-polarization and relativistic effects [8] on atomic density functional total energies and ionization energies.

In this work, we compare the published values of these total and (first) ionization energies of all-electron atoms to two existing codes in order to establish a baseline of comparison. We then extend these studies to the meta-generalized gradient and exact-exchange and hybrid levels of exchange-correlation approximation, investigating the effects of these additional levels of complexity on the total energies and ionization energies of atoms calculated using a grid basis, comparing ionization energy to experiment. Finally, we also investigate the effect of combining relativistic effects in both scalar-relativistic and fully relativistic calculations to these energies using the same levels of exchange-correlation approximation.

## 2. Method

Quantum ESPRESSO [11] [12] is “an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modeling at the nanoscale, based on density-functional theory, plane waves, and pseudopotentials” that includes an atomic density-functional code atomic OPIUM [13] is a stand-alone pseudopotential generation code that implements both density functional and Hartree-Fock theory to calculate electronic total energies. Both atomic and OPIUM use a radial grid to represent the single-particle Kohn-Sham states that is of the form:

$$r_n = a \left( e^{b(n-1)} - 1 \right) \quad (1)$$

where the parameters  $a$  and  $b$  determine the relationship of the  $N$  points that are indexed from  $n = 1$  to  $N + 1$ . In atomic,  $a$  by default is set to  $1/Z$  where  $Z$  is the atomic number of the atom being simulated, and, in OPIUM,  $a$  defaults to  $(10/Z)^{1/3}/10$ . In both codes,  $b$  is an exponential grid spacing parameter.

As of Quantum ESPRESSO version 6.3, atomic includes support for a variety of exchange-correlation functionals at the local-density approximation (LDA) and generalized-gradient approximation (GGA) levels while, at version 4.1, OPIUM implements exchange-correlation functionals at the LDA and GGA levels as well as the Hartree-Fock [14] (HF) and hybrid (PBE0) [15] functional levels. Yao and Kanai [16] implemented the TPSS [17] and SCAN [18] meta-GGA exchange-correlation functionals in a modified version of atomic. In this investigation, electronic orbital occupation of the Kohn-Sham states was chosen to

match the ground-state electron configurations of the atoms established by experiment [19].

### 3. Results

#### 3.1. Total Energy

To corroborate the existing implementations of exchange-correlation in atomic and OPIUM against the published values, **Table 1** presents the mean absolute relative error of the DFT total energies produced by the atomic and OPIUM codes from the published values for LDA/LSD (local spin density) [8] [20] and LDA & GGA [22] exchange-correlation functionals. The atomic data use the internal exchange-correlation functional implementation in Quantum ESPRESSO, and tests using the libxc [27] implementations of exchange-correlation in Quantum ESPRESSO produce statistically indistinguishable differences. **Table 2** shows the mean absolute relative error of the HF total energies produced by the OPIUM code from prior published values [28] [29].

The NIST data are reported to  $10^{-6}$  Ha so a difference of  $9 \times 10^{-7}$  Ha for the smallest total energy ( $E(\text{H}) [\text{LDA}] = -0.445671$  Ha) would produce the largest possible absolute relative error of  $2 \times 10^{-6}$ . The calculated LDA MAREs for both atomic and OPIUM are below this threshold, and the atomic LSD MARE also

**Table 1.** Mean absolute relative error (MARE) for the data in each reference for atomic code in Quantum ESPRESSO [11] [12] and the OPIUM code [13], for varying exchange-correlation functionals and spin-polarization treatment. The NIST [8] [19] [20] data use the Vosko-Wilk-Nusair [21] (VWN) parameterization of the local density approximation (LDA) while the Lee and Martin [22] data use the Perdew-Zunger [23] parameterization for LDA. Lee and Martin compare two generalized-gradient approximations (GGAs), Perdew-Wang 1991 [24] (PW91) and Perdew-Burke-Ernzerhof [25] [26] (PBE).

	atomic		OPIUM	
	NIST	Lee & Martin	NIST	Lee & Martin
LDA-VWN	0.00000000	0.000032 (51)	0.00000002	0.000035 (51)
LSD-VWN	0.00000000	-	-	-
GGA-PW91	-	0.000019 (50)	-	0.000019 (50)
GGA-PBE	-	0.000008 (50)	-	0.000008 (50)

**Table 2.** Mean error (ME), mean absolute error (MAE), mean relative error (MRE), and mean absolute relative error (MARE) for the total energy using the Hartree-Fock method in the OPIUM code with respect to the values reported in Davidson *et al.* [28] for elements  $Z = 3 - 10$ .

ME	0.0217
MAE	0.0217
MRE	0.0004
MARE	0.0004

lies below this threshold (the spin-polarized VWN functional is not implemented in OPIUM).

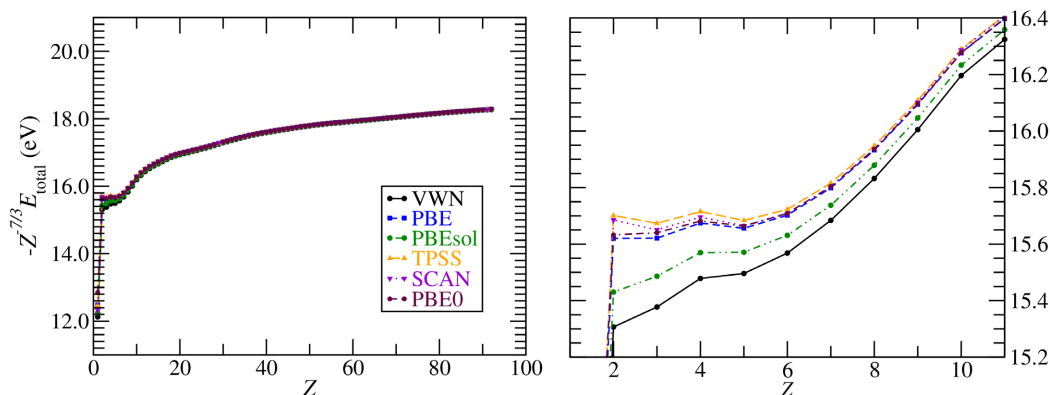
The data of Lee and Martin are reported to  $10^{-3}$  Ry so a difference of  $9 \times 10^{-4}$  Ry for the total energy of hydrogen would produce the largest possible absolute relative error of  $1 \times 10^{-3}$ . The calculated LDA, PW91, and PBE MAREs for both atomic and OPIUM lie below this threshold.

Davidson *et al.* [2] report Hartree-Fock energies to  $10^{-6}$  Ha calculated using Slater-type orbitals with an  $11s, 10p, 9d, 8f, 6g, 4h, 2i$  basis set. A comparison with Hartree-Fock calculations using the exponential radial grid in OPIUM shows mean relative and mean absolute relative errors of 0.04%, greater than the 0.0001% difference that would be produced by  $9 \times 10^{-7}$  Ha difference on the smallest total energy in this set ( $E(\text{Li})$  [HF] = -7.432727 Ha). The values for  $Z = 6 - 8$  deviate in the 0.05% - 0.2% range while the values for  $Z = 3 - 5, 9 - 10$  deviate on the order of  $1 \times 10^{-6}$  %, implying that the only numerically significant difference lies in the total energies for C, N, and O.

For completeness, we present the total energies for elements  $Z = 1 - 92$  in **Tables A1-A7** of the Appendix calculated using the DFT exchange-correlation functionals LDA-PW, GGA-PBE, GGA-PBESol, metaGGA-TPSS, metaGGA-SCAN, and hybrid-PBE0 together with Hartree-Fock.

Following Kotochigova *et al.*, we plot  $-Z^{7/3}E_{\text{total}}$  against  $Z$  to contrast the DFT exchange-correlation functionals with Hartree-Fock (**Figure 1**). At the global level, all of these methods follow the same trend. Zooming in on the  $Z = 2 - 10$  region, we see the LDA energies lowest followed by the GGA-PBESol energies, and the GGA-PBE, metaGGA-TPSS, metaGGA-SCAN, and hybrid PBE0 energies converging at this scale for  $Z > 5$ .

In addition to the atomic number-scaled total energies, we plot the relative difference from the corrected Thomas-Fermi energy (**Figure 2**). For this quantity, the differences between the functionals appear most starkly in low  $Z$  elements. In Period 3, the metaGGA functions group with the largest relative difference, followed by GGA-PBE and hybrid-PBE0. The reduced gradient expansion coefficient in both the exchange and correlation components of GGA-PBESol

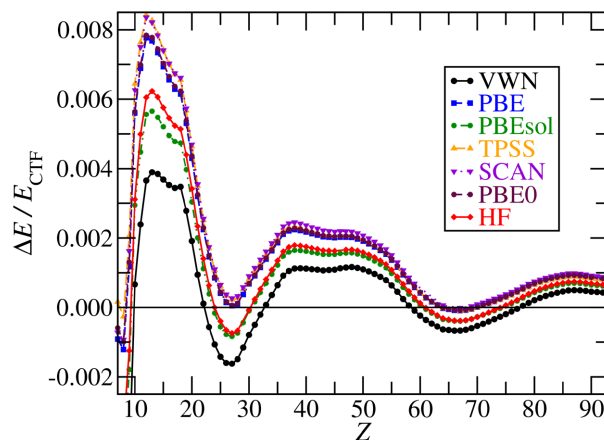


**Figure 1.** Scaled total energy  $-Z^{7/3}E_{\text{total}}$  with atomic number  $Z$  for all methods for all atoms (left) and Period 2 atoms (right).

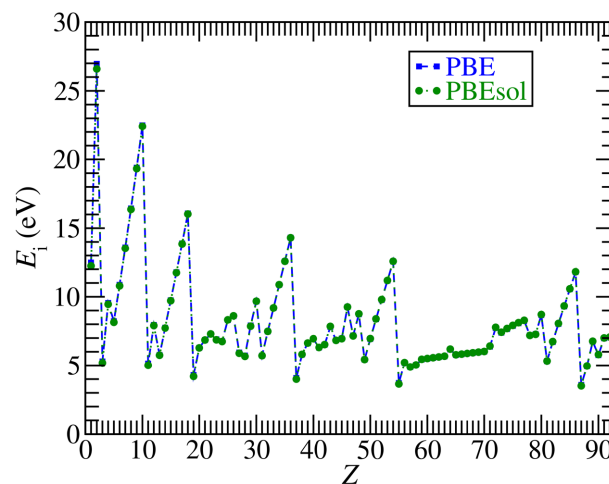
compared to GGA-PBE makes its relative differences from the corrected Thomas-Fermi energy closer to the LDA-VWN values.

### 3.2. Ionization Energy

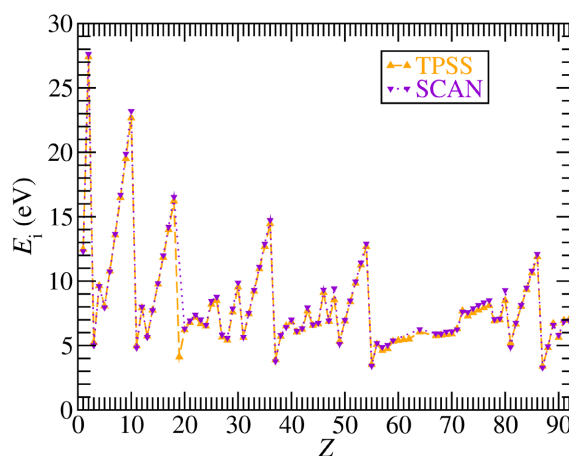
The (first) ionization energy of an atom is calculated from the difference between the total energies of the all-electron atom and the singly ionized cation [30]. The density functional theory values for ionization energy reproduce the qualitative trends of the experimentally determined values [8], and including gradient and higher-order corrections does not significantly alter these trends (see **Figures 3-5**). Ionization energies rise across each period of elements, starting low in Group 1 and rising to a peak in Group 18, before dropping for the Group 1 element in the subsequent period. For increasing  $Z$  across Groups 4 - 12, ionization energy shows fluctuations of up to nearly 5 eV reflecting the complexities of the  $d$ - and  $f$ -shell orbital energies in both the neutral atom and the singly ionized cation.



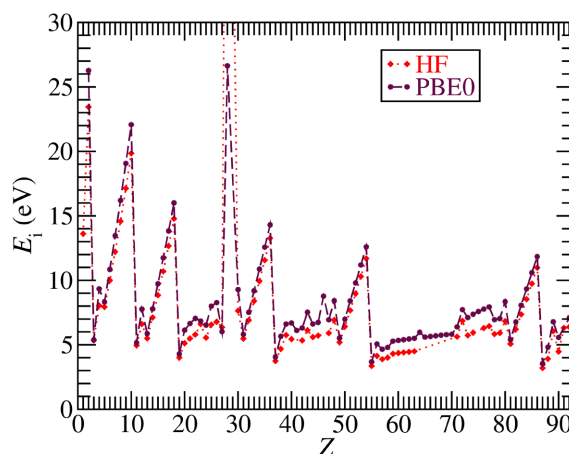
**Figure 2.** Relative difference of total energy from corrected Thomas-Fermi energy  $\Delta E/E_{CTF}$  with atomic number  $Z$  for all methods.



**Figure 3.** Ionization energy  $E_i$  with atomic number  $Z$  for two GGA functionals: PBE and PBEsol.



**Figure 4.** Ionization energy  $E_i$  with atomic number  $Z$  for two meta-GGA functionals: TPSS and SCAN.



**Figure 5.** Ionization energy  $E_i$  with atomic number  $Z$  for Hartree-Fock and the hybrid PBE0 functional.

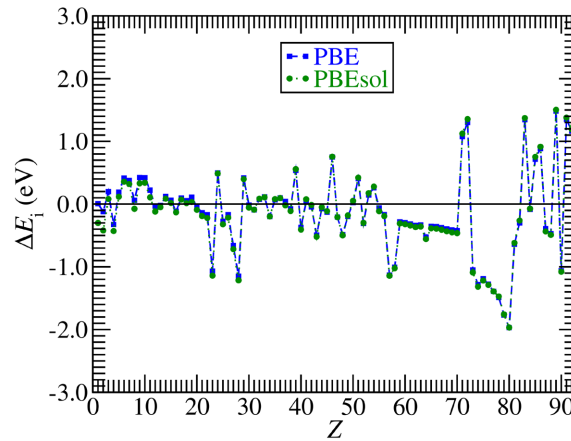
### 3.2.1. Comparison to Experiment

For more detailed consideration of the calculated ionization energies, we investigate the difference of the calculated ionization energy from the experimental values with increasing atomic number (**Figures 6-8**) as reported in the NIST Computational Chemistry Comparison and Benchmark Database [31]. We collate into **Figure 9** the comparison of the differences using all of these levels of theory. The mean-field approximation of density functional theory shows up with peak differences occurring at  $Z = 2, 27, 28, 78, 79$  and Group 16 & 17 elements, the difference from experiment trending downward with increasing  $Z$  without any attention to relativistic effects in the calculation (we consider these effects in Section 3.2.2).

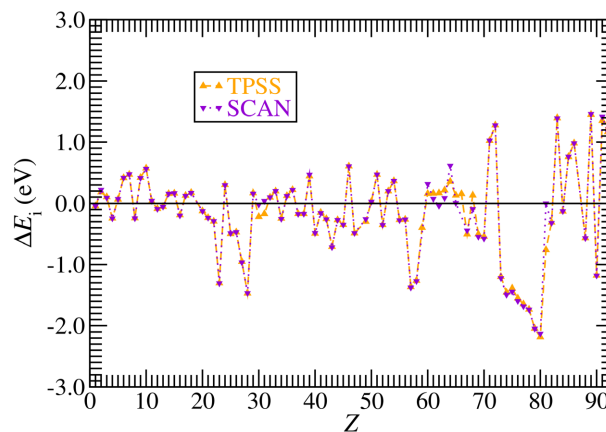
### 3.2.2. Relativistic Effects

The effects of special relativity on the electrons can be accounted for by transforming the Kohn-Sham equations into Dirac-like equations with a spinor containing two components, each indexed by the quantum numbers  $n$ ,  $\ell$ , and  $j$

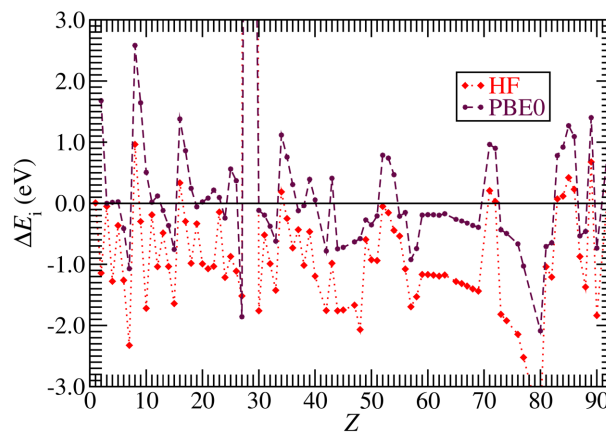
where  $j$  is the total angular momentum. These equations are coupled first-order equations of the spinor components containing the Dirac quantum number  $\kappa$ , and the charge density is constructed by summing the sum of the squares of the



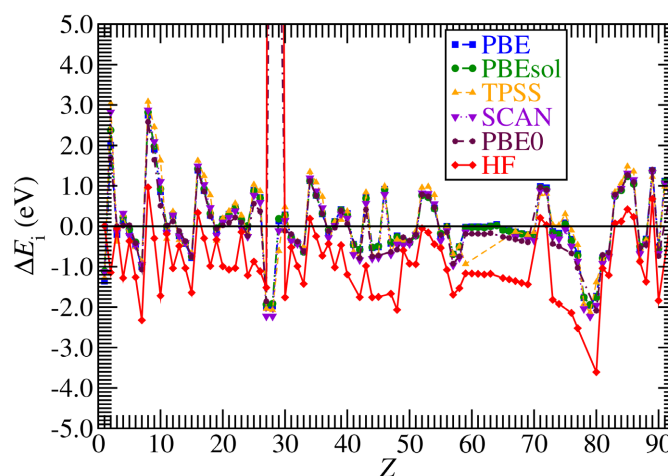
**Figure 6.** Difference in ionization energy from experiment  $\Delta E_i$  versus atomic number  $Z$  for two GGA functional.



**Figure 7.** Difference in ionization energy from experiment  $\Delta E_i$  versus atomic number  $Z$  for two meta-GGA functional.



**Figure 8.** Difference in ionization energy from experiment  $\Delta E_i$  versus atomic number  $Z$  for HF and the PBE0 functional.



**Figure 9.** Difference in ionization energy from experiment  $\Delta E_i$  versus atomic number  $Z$  for HF and the PBE, PBEsol, TPSS, SCAN, and PBE0 functionals.

**Table 3.** Mean absolute relative error (MARE) for the ionization energy with respect to the experimental values for elements  $Z = 1 - 36$ , varying relativistic treatment and exchange-correlation functional.

	None	Scalar	Full
LDA-PW	0.073	0.073	0.070
GGA-PBE	0.029	0.024	0.065
GGA-PBEsol	0.029	0.025	0.067

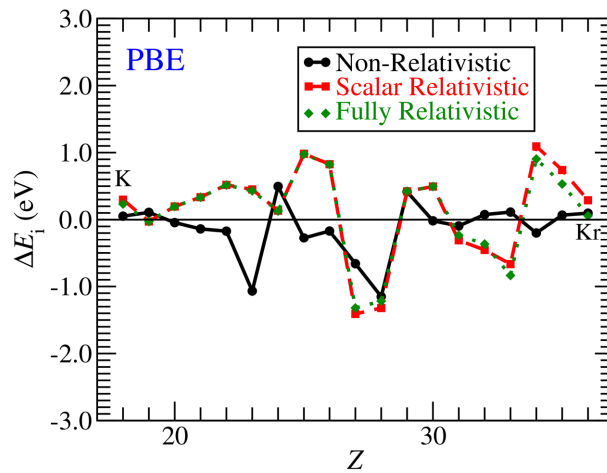
**Table 4.** Mean absolute relative error (MARE) for the ionization energy with respect to the experimental values for elements  $Z = 37 - 92$ , varying relativistic treatment and exchange-correlation functional.

	None	Scalar	Full
LDA-PW	0.068	0.081	0.065
GGA-PBE	0.073	0.063	0.046
GGA-PBEsol	0.074	0.066	0.049

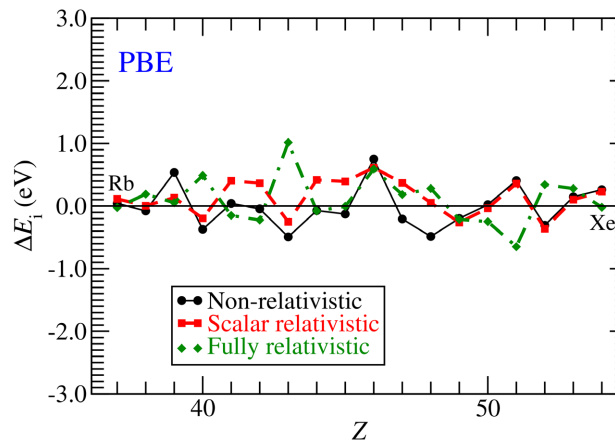
spinor components, multiplied by the occupancies and divided by the spherical surface area, over the quantum numbers  $n$ ,  $\ell$ , and  $j$ . This is the so-called fully relativistic treatment. A simplification reduces the coupled first-order equations into a single second-order equation for the large spinor component and averages over the spin-orbit components—this is the scalar relativistic case.

In **Figures 10-12**, we show the effects of the two models of relativity together with the non-relativistic calculations on the difference of calculated and experimental ionization energies for elements in periods four, five, and six ( $Z = 19 - 36$ ,  $37 - 54$ , and  $55 - 86$ , respectively) using the GGA-PBE functional. The qualitative ordering of the three calculations on each particular element remain the same in LDA-PW and GGA-PBEsol as in GGA-PBE.

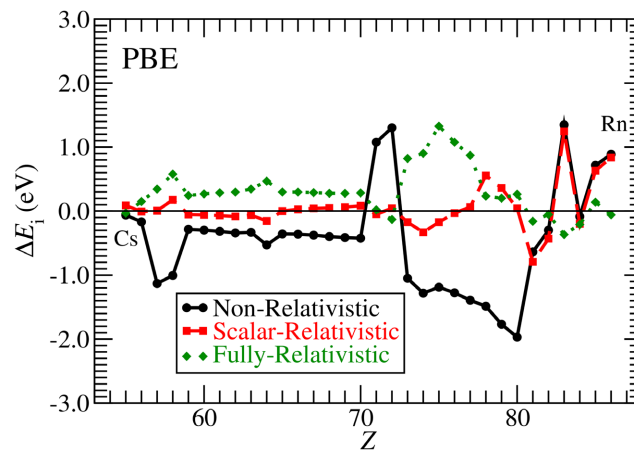




**Figure 10.** Difference in ionization energy  $\Delta E_i$  from experiment with atomic number  $Z$  for Period 4 elements ( $Z = 19 - 36$ ) using the PBE exchange-correlation functional varying relativistic treatment.



**Figure 11.** Difference in ionization energy  $\Delta E_i$  from experiment with atomic number  $Z$  for Period 5 elements ( $Z = 37 - 54$ ) using the PBE exchange-correlation functional varying relativistic treatment.



**Figure 12.** Difference in ionization energy  $\Delta E_i$  from experiment with atomic number  $Z$  for Period 6 elements ( $Z = 55 - 86$ ) using the PBE exchange-correlation functional varying relativistic treatment.

## 4. Conclusion

We present density functional atomic total energies for an exponential radial grid basis using exchange-correlation approximations ranging from local density through generalized gradient and meta-generalized gradient to exact-exchange hybrid levels of complexity in comparison with the same energies calculated using the Hartree-Fock method. We demonstrate that, while these increased levels of complexity change the absolute energies and first ionization energies of the atoms, the relative trends with increasing atomic number and difference from experiment remain largely the same. Adding scalar and spinor relativistic corrections to the density-functional Hamiltonian can alter significantly the difference of the first ionization energy from experiment, changing the sign of the difference, but the mean absolute relative error in the first ionization energy for elements  $Z = 37 - 92$  reduces only from 7% to 5%.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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## Appendix—Total Energies

**Table A1.** Total spin-polarized energies (in Ha) for atoms in the first two periods of the periodic table ( $Z = 1 - 10$ ) with varying exchange-correlation functionals (as well as DFT to HF) and no relativistic correction. Values are depicted to  $10^{-4}$ , indicative of the digit where no grid basis error is evident.

Elements	PW	PBE	PBEsol	TPSS	SCAN	HF	PBE0
H	-0.4787	-0.5000	-0.4887	-0.4978	-0.4981	-0.5000	-0.4723
He	-2.8345	-2.8929	-2.8577	-2.9063	-2.9096	-2.8616	-2.8952
Li	-7.3433	-7.4622	-7.3976	-7.4836	-7.4881	-7.4327	-7.4606
Be	-14.4465	-14.6300	-14.5323	-14.6655	-14.6711	-14.5730	-14.6366
B	-24.3525	-24.6054	-24.4723	-24.6473	-24.6539	-24.5291	-24.6079
C	-37.4683	-37.7937	-37.6235	-37.8458	-37.8530	-37.6597	-37.7644
N	-54.1344	-54.5358	-54.3270	-54.6034	-54.6110	-54.2962	-54.4387
O	-74.5248	-75.0010	-74.7492	-75.0723	-75.0799	-74.7692	-74.9615
F	-99.1112	-99.6657	-99.3701	-99.7508	-99.7583	-99.4093	-99.6628
Ne	-128.2299	-128.8665	-128.5258	-128.9725	-128.9798	-128.5471	-128.8718

**Table A2.** Total spin-polarized energies (in Ha) for atoms in the third period of the periodic table ( $Z = 11 - 18$ ) with varying exchange-correlation functionals (as well as DFT to HF) and no relativistic correction. Values are depicted to  $10^{-4}$ , indicative of the digit where no grid basis error is evident.

Elements	PW	PBE	PBEsol	TPSS	SCAN	HF	PBE0
Na	-161.4436	-162.1732	-161.7843	-162.2979	-162.2967	-161.8589	-162.1800
Mg	-199.1353	-199.9557	-199.5177	-200.0925	-200.0907	-199.6146	-199.9708
Al	-241.3166	-242.2326	-241.7460	-242.3799	-242.3780	-241.8767	-242.2483
Si	-288.2178	-289.2327	-288.6965	-289.3935	-289.3916	-288.8346	-289.2323
P	-340.0001	-341.1164	-340.5298	-341.2942	-341.2921	-340.6489	-341.0811
S	-396.7382	-397.9468	-397.3101	-398.1362	-398.1337	-397.4785	-397.9523
Cl	-458.6655	-459.9715	-459.2838	-460.1754	-460.1723	-459.4821	-460.0026
Ar	-525.9398	-527.3470	-526.6072	-527.5691	-527.5654	-526.8175	-527.3884

**Table A3.** Total energies for atoms (in Ha) in the fourth period of the periodic table ( $Z = 19-36$ ) with varying exchange-correlation functionals (as well as DFT to HF) and no relativistic correction.

Elements	PW	PBE	PBEsol	TPSS	SCAN	HF	PBE0
K	-598.1992	-599.7111	-598.9171	-599.9402	-599.9368	-599.1648	-599.7514
Ca	-675.7353	-677.3495	-676.5013	-677.5859	-677.5821	-676.7582	-677.3925
Sc	-758.6778	-760.3916	-759.4911	-760.6306	-760.6267	-759.7357	-760.4263
Ti	-847.2954	-849.1098	-848.1569	-849.3527	-849.3488	-848.3701	-849.1210
V	-941.7335	-943.6496	-942.6440	-943.8973	-943.8932	-942.8037	-943.6192
Cr	-1042.2086	-1044.2318	-1043.1756	-1044.4882	-1044.4841	-1043.1418	-1044.0567

## Continued

Mn	-1148.6341	-1150.7570	-1149.6448	-1151.0155	-1151.0115	-1149.6259	-1150.5819
Fe	-1261.2130	-1263.4331	-1262.2665	-1263.6892	-1263.6850	-1262.2909	-1263.3215
Co	-1380.1565	-1382.4750	-1381.2542	-1382.7323	-1382.7278	-1381.3084	-1382.4160
Ni	-1505.6038	-1508.0221	-1506.7470	-1508.2821	-1508.2776	-1506.8158	-1508.0017
Cu	-1637.7812	-1640.2999	-1638.9720	-1640.5665	-1640.5615	-1638.8261	
Zn	-1776.5615	-1779.1840	-1777.7991	-1779.4510	-1779.4528	-1777.8481	-1779.1917
Ga	-1921.8390	-1924.5717	-1923.1302	-1924.8402	-1924.8345	-1923.2610	-1924.5950
Ge	-2073.8164	-2076.6615	-2075.1637	-2076.9344	-2076.9285	-2075.3404	-2076.6819
As	-2232.5731	-2235.5331	-2233.9783	-2235.8126	-2235.8067	-2234.1722	-2235.5330
Se	-2398.1209	-2401.1849	-2399.5729	-2401.4663	-2401.4598	-2399.8432	-2401.2316
Br	-2570.6124	-2573.7847	-2572.1159	-2574.0707	-2574.0637	-2572.4413	-2573.8628
Kr	-2750.1333	-2753.4175	-2751.6911	-2753.7104	-2753.7028	-2752.0550	-2753.5126

**Table A4.** Total energies (in Ha) for atoms in the fifth period of the periodic table ( $Z = 37 - 54$ ) with varying exchange-correlation functionals (as well as DFT to HF) and no relativistic correction.

Elements	PW	PBE	PBEsol	TPSS	SCAN	HF	PBE0
Rb	-2936.3271	-2939.7267	-2937.9402	-2940.0142	-2940.0063	-2938.3575	-2939.8257
Sr	-3129.4380	-3132.9502	-3131.1038	-3133.2324	-3133.2241	-3131.5457	-3133.0557
Y	-3329.5096	-3333.1348	-3331.2302	-3333.4091	-3333.4004	-3331.6842	-3333.2392
Zr	-3536.7411	-3540.4818	-3538.5186	-3540.7494	-3540.7403	-3538.9687	-3540.5734
Nb	-3751.2785	-3755.1461	-3753.1248	-3755.4104	-3755.4009	-3753.4914	-3755.1528
Mo	-3973.1449	-3977.1347	-3975.0527	-3977.3965	-3977.3867	-3975.3687	-3977.0887
Tc	-4202.3077	-4206.4089	-4204.2647	-4206.6637	-4206.6532	-4204.6068	-4206.3803
Ru	-4439.0262	-4443.2398	-4441.0368	-4443.4919	-4443.4816	-4441.4559	-4443.2971
Rh	-4683.3162	-4687.6451	-4685.3816	-4687.8918	-4687.8813	-4685.8370	-4687.7389
Pd	-4935.3493	-4939.7953	-4937.4708	-4940.0419	-4940.0305	-4909.4362	-4939.9225
Ag	-5195.0177	-5199.5836	-5197.1976	-5199.8231	-5199.8116	-5197.6985	-5199.7176
Cd	-5462.3711	-5467.0536	-5464.6051	-5467.2847	-5467.2819	-5465.1331	-5467.1988
In	-5737.2935	-5742.0973	-5739.5870	-5742.3212	-5742.3085	-5740.1692	-5742.2507
Sn	-6019.9514	-6024.8778	-6022.3066	-6025.0973	-6025.0841	-6022.9142	-6025.0248
Sb	-6310.3978	-6315.4485	-6312.8160	-6315.6650	-6315.6513	-6313.4262	-6315.5752
Te	-6608.6290	-6613.7934	-6611.0995	-6614.0024	-6613.9883	-6611.7627	-6613.9567
I	-6914.7563	-6920.0375	-6917.2830	-6920.2414	-6920.2273	-6917.9809	-6920.2243
Xe	-7228.8342	-7234.2354	-7231.4198	-7234.4357	-7234.4210	-7232.1384	-7234.4337

**Table A5.** Total energies (in Ha) for atoms in the sixth period of the periodic table without the lanthanoids ( $Z = 55 - 56$  &  $72 - 86$ ) with varying exchange-correlation functionals (as well as DFT to HF) and no relativistic correction.

Elements	PW	PBE	PBEsol	TPSS	SCAN	HF	PBE0
Cs	-7550.5395	-7556.0620	-7553.1835	-7556.2439	-7556.2341	-7553.9337	-7556.2604
Ba	-7880.0891	-7885.7318	-7882.7904	-7885.8984	-7885.8879	-7883.5438	-7885.9309
Hf	-14317.4817	-14324.9934	-14321.0739	-14324.8088	-14324.7918	-14321.2240	-14325.0883
Ta	-14795.8960	-14803.5317	-14799.5493	-14803.3298	-14803.3121	-14799.7544	-14803.6232
W	-15283.4952	-15291.2573	-15287.2113	-15291.0392	-15291.0206	-15287.4496	-15291.3311
Os	-16286.3431	-16294.3520	-16290.1777	-16294.1022	-16294.0826	-16290.5398	-16294.4628
Ir	-16801.6903	-16809.8191	-16805.5815	-16809.5544	-16809.5347	-16806.0392	-16809.9879
Pt	-17326.5569	-17334.8107	-17330.5104	-17334.5384	-17334.5197	-17331.0655	-17335.0387
Au	-17860.7629	-17869.1433	-17864.7784	-17868.8584	-17868.8392	-17865.4001	-17869.3994
Hg	-18404.2404	-18412.7448	-18408.3140	-18412.4409	-18412.4234	-18408.9915	-18413.0201
Tl	-18956.9279	-18965.5609	-18961.0646	-18965.2388	-18965.2180	-18961.8248	-18965.8529
Pb	-19518.9760	-19527.7388	-19523.1781	-19527.4010	-19527.3793	-19523.9912	-19528.0332
Bi	-20090.4187	-20099.3129	-20094.6875	-20098.9607	-20098.9386	-20095.5302	-20099.5965
Po	-20671.2387	-20680.2541	-20675.5636	-20679.8835	-20679.8609	-20676.4807	-20680.5789
At	-21261.5242	-21270.6638	-21265.9091	-21270.2770	-21270.2537	-21266.8817	-21271.0170
Rn	-21861.3113	-21870.5778	-21865.7588	-21870.1760	-21870.1519	-21866.7722	-21870.9481

**Table A6.** Total energies for lanthanoid atoms in the sixth period of the periodic table ( $Z = 57-71$ ) with varying exchange-correlation functionals (as well as DFT to HF) and no relativistic correction.

Elements	PW	PBE	PBEsol	TPSS	SCAN	HF	PBE0
La	-8217.5565	-8223.3205	-8220.3173	-8223.4711	-8223.4601	-8221.0667	-8223.5150
Ce	-8563.3496	-8569.2294	-8566.1658	-8569.3575	-8569.3463	-8566.8484	-8569.4036
Pr	-8917.6918	-8923.6851	-8920.5618	-8923.7868	-8924.7249	-8921.0634	-8923.7892
Nd	-9280.2979	-9286.5632	-9283.3036	-9286.4577	-9287.3806	-9283.7003	-9286.5391
Pm	-9651.6112	-9657.8410	-9654.5956	-9657.7232	-9658.6603	-9654.8642	-9657.8147
Sm	-10031.4581	-10037.8069	-10034.5001	-10037.5908	-10038.5452	-10034.6311	-10037.6932
Eu	-10419.9970	-10426.4656	-10423.0972	-10426.1353	-10427.1106	-10423.0761	-10426.2490
Gd	-10816.9890	-10823.5771	-10820.1467	-10823.5837	-10823.5704	-10820.1271	-10823.3250
Tb	-11223.0809	-11229.7743	-11226.2853	-11710.0870	-11230.5828	-11226.3007	-11229.6909
Dy	-11637.9502	-11644.7573	-11641.2077	-12158.4238	-11645.6381	-11641.2295	-11644.7255
Ho	-12061.8042	-12068.7258	-12065.1154	-12068.6458	-12068.6311	-12065.1352	-12068.7345
Er	-12494.7175	-12501.7546	-12498.0831	-12501.6519	-12501.6367	-12498.0921	-12501.7918
Tm	-12936.7644	-12943.9179	-12940.1850	-12943.7930	-12943.7767	-12940.1744	-12943.9711
Yb	-13388.0190	-13395.2897	-13391.4951	-13395.1432	-13395.1241	-13391.4562	-13395.3453
Lu	-13848.2048	-13855.5951	-13851.7380	-13855.4286	-13855.4122	-13851.8080	-13855.6783

**Table A7.** Total energies (in Ha) for atoms in the seventh period of the periodic table up to U ( $Z = 87-92$ ) with varying exchange-correlation functionals and no relativistic correction.

Elements	PW	PBE	PBEsol	TPSS	SCAN	HF	PBE0
Fr	-22470.2876	-22479.6839	-22474.7978	-22479.2553	-22479.2304	-22475.8587	-22480.0581
Ra	-23088.6521	-23098.1757	-23093.2231	-23097.7207	-23097.6948	-23094.3037	-23098.5550
Ac	-23716.4644	-23726.1165	-23721.0987	-23725.6353	-23725.6087	-23722.1921	-23726.4962
Th	-24353.8106	-24363.5942	-24358.5107	-24363.0880	-24363.0609	-24359.6011	-24363.9642
Pa	-25001.2830	-25011.1905	-25006.0428	-25010.6519	-25010.6243	-24963.6722	-24968.0673
U	-25658.4367	-25668.4741	-25663.2607	-25667.9087	-25667.8805	-25664.2094	-25668.7856