Leading Correction to the Local Density Approximation for Exchange in Large-math xmlns="http://www.w3.org/1998/Math/MathML" display="inline">mi>Z/mi>/math> Atoms

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Leading correction to the local density approximation for exchange in large-Z atoms

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The large-Z asymptotic expansion of atomic energies has been useful in determining exact conditions for corrections to the local density approximation in density functional theory. The necessary correction is fit well with a leading $Z\ln Z$ term, and we give its coefficient. The gradient expansion approximation also has such a term, but with a smaller coefficient. Analytic results in the limit of vanishing interaction with hydrogenic orbitals (a Bohr atom) lead to the conjecture that the coefficients are precisely 2.7 times larger than their gradient expansion counterparts, yielding an analytic expression for the exchange-energy correction which is accurate to $\sim 5\%$ for all Z.

For almost a century, the non-relativistic semiclassical expansion of the total binding energy of atoms[1] has guided the development of density functional approximations, beginning with Thomas-Fermi (TF) theory[2, 3] and the local density approximation (LDA) for exchange[4, 5]. In the seventies, Lieb and Simon proved[6] that the dominant term in that expansion is given exactly by TF theory, and in the eighties Schwinger and Englert showed explicitly that the LDA recovers the dominant term for the atomic exchange energy[7–9]. Recent analytic and numerical evidence shows the same is true for atomic correlation energies[10, 11].

For exchange, recent focus has been on the leading correction to LDA[12, 13]. Most modern generalized gradient approximations (GGAs) — the starting point of most modern XC approximations — yield a well-defined correction that can be compared to atomic data for large Z. The popular approximations of PBE[14] and B88[15] both yield highly accurate approximations to this term for atoms, which are about double that of the gradient-expansion approximation[16, 17] (GEA), yielding some of the insight behind PBEsol[18]. The behavior for large Z has been built into several recent non-empirical approximations (SCAN[19], APBE[20], acGGA[11]).

The original works[12, 13] on expanding the beyond-LDA exchange energy for atoms,

$$\Delta E_{\rm x} = E_{\rm x} - E_{\rm x}^{\rm LDA}\,, \qquad (1)$$

used simple powers of $Z^{1/3}$, based on the scaling behavior of the gradient expansion for the slowly-varying electron gas. Here we provide three lines of evidence for the existence of a $Z\ln Z$ contribution, showing that the analytic forms used as 'exact conditions' are likely incorrect, and should be replaced by those suggested below. Thus, the current work not only contributes to the very long-standing search for the expansion of the energy of atoms in mathematical physics, but also provides a crucial correction to exact conditions which are built into the latest modern density functional approximations, used throughout condensed matter physics, materials science, and chemistry.

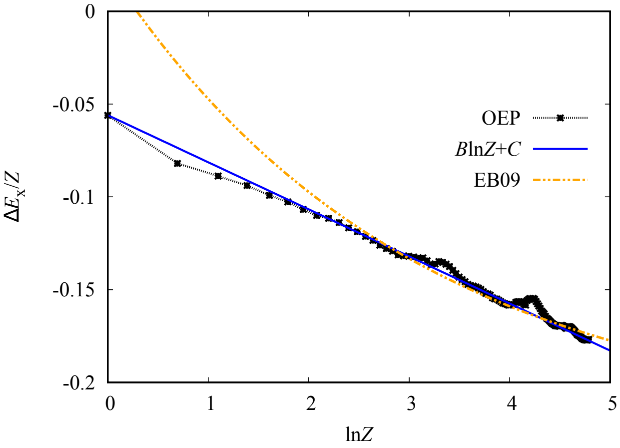

FIG. 1. Beyond-LDA exchange energy per electron ($\Delta E_{\rm x}/Z$) of neutral atoms. The solid blue line is the new $B\ln Z + C$ fit described in the text, whereas the orange dashed curve is the fit of Ref. [13]. (Hartree atomic units used throughout.)

Our first line of inquiry consists of evaluating $\Delta E_{\rm x}/Z$ for neutral atoms up to $Z = 120$, using the optimized effective potential (OEP). These data are plotted versus $\ln Z$ in Fig. 1, and a straight line gives a significantly better fit than Ref. [13].

A second direction shows analytically that applying the GEA to the TF density profile for an atom [21] produces a ln$Z$ divergence near the nucleus, but its coefficient is less than half the slope of the fit in Fig. 1, reflecting the aforementioned discrepancy with GGAs.

A third direction is a study of the Bohr atom[22], in which the electron repulsion is infinitesimal and the orbitals are hydrogenic. Exchange energies were calculated analytically for such atoms with up to 22 closed shells[23]. Fitting these, as well as the LDA exchange energies, gives a Zln$Z$ coefficient larger than that of neutral, interacting-electron atoms. In GEA, the cusp where the Bohr-atom TF density abruptly vanishes also contributes. Overall, the Zln$Z$ coefficient is here 2.7 times larger than in GEA. Assuming that ratio is true for all atoms explains the data of Fig. 1.

Our first step is a detailed analysis of Fig. 1. Three candidates for the leading correction to LDA are: a term proportional to Z [13], the Zln$Z$ dependence suggested by the GEA, and a term proportional to $Z^{4/3}$, which appears in the oscillations across the periodic table.[24] The general form

$$\Delta E_{\rm X}/Z \approx -A'\ Z^{1/3} - B{\rm ln}Z - C - DZ^{-1/3} \qquad (2)$$

enables a discussion of all these possibilities.

We use the OPMKS code [25] to calculate $E_{\rm X}$ with the OEP and $E_{\rm X}^{\rm LDA}$ with the spin-dependent LDA of [26], for non-relativistic neutral atoms up to $Z = 120$, extending an earlier data set.[10] To avoid bias, we ignore the large numbers of highly correlated data points across subshells, keeping only atoms with closed subshells, grouped as follows: He and the alkaline earths (s), the remaining noble gases (p), group 12 metals (d), and closed f-shell atoms. There are 20 such atoms for $Z \leq 120$, but we exclude the first element of each group ($Z = 2$, 10, 30, and 70), as these are most strongly affected by oscillations in Z.[10]

To generate a set of competing models for our data, we vary a subset of coefficients in Eq. (2), holding the others to zero, and find the coefficients and their standard errors from nonlinear regression using the Levenberg-Marquardt method. [27] These are shown in Table I, listed in order of the number of parameters, with data entries for zeroed out coefficients left blank. The final column shows the reduced χ^2 of the fit, i.e., the sum of the squared errors per degree of freedom, $\chi^2_{\rm red} = \sum_{i=1}^{n}\left(\frac{\delta_i}{\sigma}\right)^2/(n-m)$. Here δ_i is the difference between the two sides of Eq. (2) for the ith value of Z, the standard error σ has been set to 1 mHa for simplicity, and m is the number of free parameters in the fit.

For the first (and worst) two forms, $\Delta E_{\rm X} \propto Z$ is the leading order, as in Ref. [13]. The logarithmic fit, line 3, has the smallest errors in coefficients and the best $\chi_{\rm red}$. This fit does remarkably well also *outside* the range of Z fitted, even down to hydrogen, as seen in Fig. 1.

	A'	B	C	D	$\chi^2_{\rm red}$
1			0.153(6)		560
2			0.2138(34)	-0.205(11)	22.1
3		0.02464(26)	0.0590(10)		0.91
4		0.0256(14)	0.053(9)	0.008(12)	0.95
5	0.0007(15)	0.0239(16)	0.0592(11)		0.96
6	0.0128(9)		0.134(5)	-0.098(7)	1.3
7	-0.007(8)	0.039(16)	0.01(5)	0.06(7)	0.98

TABLE I. Coefficients of various fits of $\Delta E_{\rm X}/Z$ in Eq. (2), with "missing" coefficients fixed at zero. $\chi^2_{\rm red}$ quantifies the errors of the fit as described in the text. Standard errors in the coefficients are given in parenthesis.

The remaining fits have additional free parameters. A $Z^{1/3}$ term (fits 5 and 7) slightly degrades the quality of the fit, in the sense that $\chi_{\rm red}$ increases ($n-m$ decreases more than $\sum_i \delta_i^2$), and the standard error of the A' coefficient is larger than its absolute value, suggesting it should be set to zero.[13] A term proportional to $Z^{-1/3}$ is likewise ineffective (fits 4 and 7). Fit 6, using only powers of $Z^{1/3}$ without a logarithmic term, results in a somewhat larger $\sum_i \delta_i^2$ despite the larger number of free parameters.

An asymptotic series should increase in accuracy as Z increases, so we refit models to a more restricted set of data: first by dropping a second element of each group (12 atoms), and then a third (9 atoms). For the ln$Z$-leading model, the three fits yield essentially the same results ($B = 0.0254, 0.0253$ and $C = 0.0560, 0.0562$). For the $Z^{1/3}$ model (fit 6), the coefficients drift noticeably as the data is restricted to a smaller range, and the fit is poor outside the range fitted, similar to the EB09 curve in Fig. 1. As a final test, using all data from $Z = 1$ to 120 indiscriminately yields coefficients for B and C that are statistically indistinguishable from those of fit 3, but with a much higher $\chi^2_{\rm red}$. The data and details of the fits are given in [28].

Overall, the fits with the ln$Z$ term as leading order are clearly the most predictive, and for best judgement of the asymptotic behavior we choose the 12-atom fit of the ln$Z$ model, which is appropriately weighted to large Z (the 9-atom fit gives larger standard errors for B and C [28]):

$$\Delta E_{\rm X} \approx -0.0254 Z{\rm ln}Z - 0.0560 Z, \qquad (3)$$

which is the curve shown in Fig. 1. Remarkably, given that $E_{\rm X}^{\rm LDA}$ is -0.2564 for hydrogen, this yields -0.3124, almost exactly matching the analytic result, $-5/16$. That the success of this fit should in fact be expected of the semiclassical approximation is evident in Figs. 1 and 9 of [10] and in [29]. Before such an asymptotic expansion diverges, the inclusion of the next term will often improve accuracy by two orders of magnitude.[29, 30] Eq. (3) thus provides another example of "the principle of unreasonable utility of asymptotic estimates."[31]

Next, we estimate $\Delta E_{\rm X}$ theoretically. The LDA exchange

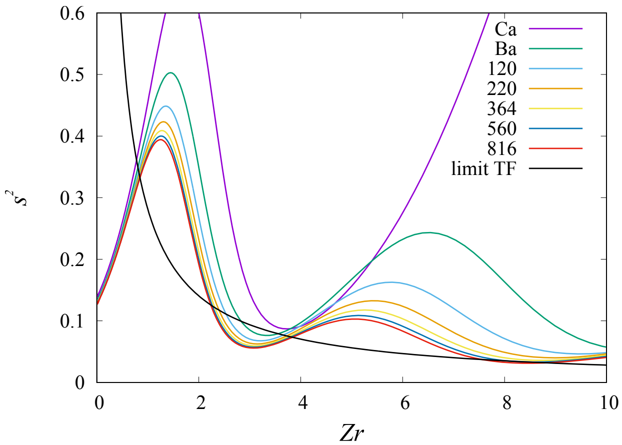

FIG. 2. Plot of s^2 near the nucleus versus distance, scaled as Zr, for alkaline earth atoms ranging from Ca up to $Z = 816$ which has valence shell 16s^2. The black line shows the TF model.

energy is given by

$$E_{\rm X}^{\rm LDA} = -a_{\rm X} \int d^3r \; n^{4/3}(\mathbf{r}) \; , \tag{4}$$

where $a_{\rm X} = 3\,(3/\pi)^{1/3}/4$ [4, 5], and insertion of the TF density[21] into this expression directly gives the dominant contribution[10] to exchange as $Z \to \infty$, $E^{\rm TF} = -A\,Z^{5/3}$. For the beyond-LDA contribution to the exchange energy, Eq. (1), we try the GEA[17, 32],

$$\Delta E_{\rm X}^{\rm GEA} = -\mu^{\rm GE} a_{\rm X} \int n^{4/3}(\mathbf{r})\, s^2(\mathbf{r})\, d^3r \; , \tag{5}$$

where $s = |\nabla n|/(2k_{\rm F} n)$ is the dimensionless gradient parameter, $k_{\rm F} = (3\pi^2)^{1/3} n^{1/3}$ is the local Fermi wavenumber, and $\mu^{\rm GE} = 10/81$.[33] Application of Eq. (5) to the slowly-varying gas, or to a neutral atom using the density scaling of [12], yields a term of order Z when scaled toward the TF limit. However, the present analysis amounts to scaling the potential, in the sense of Refs. [34, 35]. While potential- and density-scaling are interchangeable for the dominant term of the large-Z asymptotic expansion (TF theory), additional terms appear for potential scaling, such as the Scott correction to the kinetic energy [21]. To show this for exchange, we proceed by directly employing the TF profile in Eq. (5).

Gradients are weak in the bulk of large atoms, with s of order $Z^{-1/3}$. At distances smaller than $O(Z^{-1/3})$ from the nucleus, screening of the nuclear charge is negligible[22] and the TF density varies as $(2Z/r)^{3/2}/3\pi^2$, so

$$s^{\rm TF}(r) \simeq \frac{3}{4}\frac{1}{\sqrt{2Zr}} \; , \qquad r \ll Z^{-1/3} \; . \tag{6}$$

This approximation fails in the region where the inner shell (1s) electrons dominate; see Fig. 2, which shows s^2 of alkaline earths up to $Z = 816$ (using FHI98PP in all-electron mode[36]) and s^2 of the TF density, Eq. (6). For $r >> 1/Z$, the atomic gradients approach the TF curve, while near $r \approx 1/Z$, the density profile displays the oscillations studied in [22] and switches over to that of the well-known nuclear cusp, while s remains finite, achieving its maximum value around $r = 1/Z$. Keeping only the divergent contribution to Eq. (5) gives:

$$\Delta E_{\rm X}^{\rm GEA} \simeq -\frac{9\mu^{\rm GE}}{8\pi^2} Z \int_{Z^{-1}}^{Z^{-1/3}} \frac{dr}{r} \; , \tag{7}$$

which yields a logarithmic term,

$$\Delta E_{\rm X}^{\rm GEA} = -\frac{3\mu^{\rm GE}}{4\pi^2} Z \ln Z + O(Z) \; . \tag{8}$$

We define

$$B = -\lim_{Z\to\infty} \Delta E_{\rm X}/(Z\ln Z) \; , \tag{9}$$

and our derivation yields

$$B^{\rm GEA} = \frac{3}{4\pi^2}\mu^{\rm GE} \tag{10}$$

or about 9.38 mHa. The presence of such a logarithmic term in the GEA for atoms was noticed in [37], and could be inferred from earlier work (see Appendix A of [11]).

We have no rationale for the difference between the results of the GEA, Eq. (10), and the actual data, Eq. (3), i.e., the slope in Fig. 1. Eq. (10) is unaffected by integration by parts (unlike [38]). Thus, the beyond-LDA exchange energy of large-Z atoms has a leading $Z\ln Z$ term both numerically and in GEA, but their coefficients disagree.

A similar analysis can be applied to the analog of Eq. (5) for the kinetic energy, leading to a stronger divergence at small r, due to the presence of an extra power of $n^{1/3}$. In addition to the naive-scaling $Z^{5/3}$ term, the small-r cutoff produces a Z^2 term, proportional to the Scott correction mentioned above. This procedure does not generate the exact coefficient, -1/2 (see [21]). Instead this is inferred from the Bohr atom,[10] to which we turn for the analysis of exchange.

The simplicity of the Bohr atom (hydrogenic orbitals) allows calculations to much larger electron number, leading to unambiguous results. We fill N hydrogenic orbitals in a potential $-N/r$, so that N plays the role of Z here. The inner region, $r << N^{-1/3}$, is identical to that of interacting atoms in the large Z limit.[39]

We analytically evaluated $E_{\rm X}$, defined by an infinitesimal Coulomb repulsion, up to $N = 7590$ (22 shells), using Mathematica.[23] Our extremely accurate fit has the form

$$E_{\rm X}^{\rm Bohr}(N) = \tag{11}$$
$$-\bar{A}_o N^{5/3} - (\bar{B}_o \ln N + \bar{C}_o)N - (\bar{D}_o \ln N + \bar{E}_o)N^{1/3} + ..,$$

where the subscript denotes a Bohr-atom coefficient and the bar denotes $E_{\rm X}$. The leading coefficient is $(2/3)^{1/3}(4/\pi^2)$,

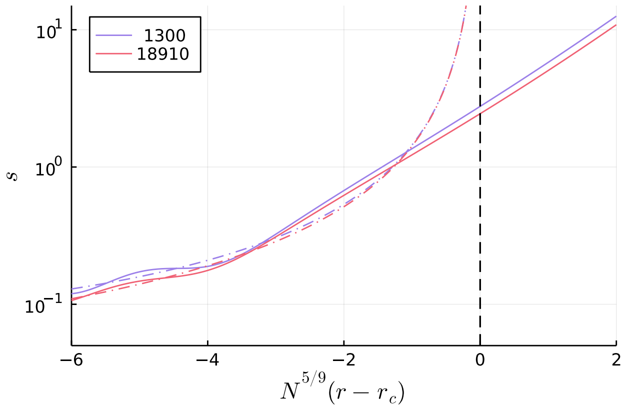

FIG. 3. Plot of the gradient parameter s near the edge of the Bohr atom, versus distance from the cusp radius r_c, scaled by $N^{5/9}$, for two representative values of N identified in the legend. Dot-dashed lines: the results of the corresponding TF models, which diverge at r_c (dashed vertical line).

from LDA applied to the TF density[39], while $\bar{B}_o = 26.268$ mHa agrees with $7/(27\pi^2)$ to 5 digits, with $\bar{C}_o = 45.3536$ mHa, $\bar{D}_o = -3.17$ mHa and $\bar{E}_o = 0.6$ mHa, determined to the number of digits shown (see [28] for details).

For LDA, there are also $O(N^{2/3}\ln N)$ and $O(N^{2/3})$ terms, making results harder to fit. However, the simplicity of the expressions[22] and availability of arbitrary precision software (using the Julia language with 64-decimal-digit accuracy) enables their brute-force evaluation for up to 100 full shells ($N = 676700$).[28] We find $B_o^{\rm LDA}$ to match $-2/(27\pi^2)$ to within $\sim 0.1\%$ (note the opposite sign), yielding

$$B_o = \bar{B}_o - B_o^{\rm LDA} = \frac{1}{3\pi^2}\,. \tag{12}$$

To evaluate the GEA, note the TF density distribution:

$$n_o^{\rm TF} = \frac{(2N)^{3/2}}{3\pi^2}\left(r^{-1}-r_c^{-1}\right)^{3/2}\,, \qquad r \le r_c\,, \tag{13}$$

where $r_c = (18/N)^{1/3}$ is the radius beyond which the density vanishes,[39] so s diverges not only at the nucleus but also as r approaches r_c [39], as

$$s_o^{\rm TF} \simeq \frac{3\,3^{2/3}}{4\,2^{1/6}}\left[N^{5/9}(r_c-r)\right]^{-3/2}\,, \quad 0<r_c-r\ll N^{-1/3}\,. \tag{14}$$

The result is

$$\Delta E_o^{\rm GEA} \simeq -\frac{9\mu^{\rm GE}}{8\pi^2}N\left[\int_{N^{-1}}^{N^{-1/3}}\frac{dr}{r}+\int_0^{r_c-N^{-5/9}}\frac{dr}{r_c-r}\right], \tag{15}$$

where the first logarithmic divergence is treated as above. The second is also cut off, taking into account that the kinetic energy is here very small, and the wavelength of the electrons is of order $N^{-5/9}$,[40] as displayed in Fig. 3. As a result, the contribution of the second divergence is 3 times smaller than that of the first, yielding

$$B_o^{\rm GEA} = \frac{\mu^{\rm GE}}{\pi^2}\,. \tag{16}$$

The two regions of divergence also determine $B_o^{\rm LDA}$. The inner region of the density has been studied in detail in [22]. The leading non-oscillatory correction to the TF density profile is $n(r) \simeq n^{\rm TF}(r)[1-1/(64Zr)]$ for $Z^{-1} \ll r \ll Z^{-1/3}$, producing a contribution of $-1/(18\pi^2)$ via Eq. (4). Consistency with the result $B_o^{\rm LDA} = -2/(27\pi^2)$, Eq. (12), requires that the outer divergence yields a contribution $1/3$ as large as the first, just as for $B_o^{\rm GEA}$.

The value excogitated from the highly precise numerical results, Eq. (12), is exactly 27/10 times larger than that of the GEA, Eq. (16). It is tempting to conjecture that

$$B = \frac{27}{10}\,B^{\rm GEA} \tag{17}$$

yields the exact result for *all* atoms, including fully interacting ones, implying that $B = 1/(4\pi^2)$ or 25.3 mHa is the exact result for neutral atoms, in agreement with our fit, Eq. (3). More generally, the conjecture gives the prediction

$$B = \frac{1}{12\pi^2}\left(4-\frac{N}{Z}\right) \tag{18}$$

for any N/Z ratio, interpolating between the result for neutral atoms, $N = Z$, and Eq. (12) for $N \ll Z$. A careful investigation of this relationship will require generating data for a large range of N for each N/Z ratio, as in Fig. 1. As a preliminary check, we show in [28] that applying this formula with a constant C to a number of positive ions with $N/Z = 1/2$ continues to give agreement with the beyond-LDA data from the OEP, at the $\sim 5\%$ level, for $N > 2$.

Last, we turn to the implications for approximate functional development. Our derivation applies to most GGA's for the exchange energy, usually written in terms of an enhancement factor $F_{\rm X}$:

$$E_{\rm X}^{\rm GGA} = -a_{\rm X}\int n^{4/3}(\mathbf{r})F_{\rm X}(s(\mathbf{r}))\,d^3r\,. \tag{19}$$

Typically, $F_{\rm X} \approx 1+\mu^{\rm GGA}s^2+\ldots$ for small s, which dominates in the TF limit. Thus Eq. (10) applies, with $\mu^{\rm GE}$ replaced by $\mu^{\rm GGA}$. This yields 16.7 mHa for PBE and 20.9 mHa for B88, differing from the value of 25.4 mH of Eq. (3). However, both yield accurate $E_{\rm X}$ for Z between 10 and 100, due to differences in the remaining terms of a large-Z fit. Thus, functionals that have been fit to large-Z data, such as SCAN, are accurate for all practical calculations. In the future both the $O(Z\ln Z)$ and the $O(Z)$ terms should be addressed in developing approximate density functionals.

Using the hydrogen atom as a 'norm'[19], the conjecture above yields:

$$\Delta E_{\rm X}^{\rm normed} = -Z\left\{\frac{\ln Z}{4\pi^2}+\frac{5}{16}-0.2564\right\} \tag{20}$$

for neutral atoms, which is indistinguishable from the straight line of Fig 1, and contains no empirical parameters.

In conclusion, the present work is a step in the process of improving DFT approximations using asymptotic expansions for non-relativistic atoms: it identifies a logarithmic divergence in the coefficient of the leading $O(Z)$ contribution to the beyond-LDA exchange energy, resulting in a leading $Z\ln Z$ term.

Further steps would involve studying existing approximations, evaluating the coefficients of both their $Z\ln Z$ terms and their $O(Z)$ terms. Obtaining very-high-Z data for real atoms is crucial, possibly using simplified methods. Analogous data for molecules and solids would also be very helpful, especially to determine any differences based on the lack of classical turning surfaces in solids[41]. But first and foremost, a derivation of the $Z\ln Z$ term from semiclassical theory, including the correct value of its coefficient, would provide a fundamental, detailed understanding of the exchange energy, and would be instrumental in guiding future developments in DFT.

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