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

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The large-Z asymptotic expansion of atomic exchange energies has been useful in determining exact conditions for corrections to the local density approximation in density functional theory. We find that the necessary correction is fit well with a leading $Z\ln Z$ term, and find its coefficient numerically. The gradient expansion approximation also displays such a term, but with a substantially smaller coefficient. Analytic results in the limit of vanishing interaction with hydrogenic orbitals (a Bohr atom) are given, leading to the conjecture that the true coefficients for all atoms are precisely 2.7 times larger than their gradient expansion counterpart. Combined with the hydrogen atom result, this yields 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 the 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). This fact produced some of the insight behind PBEsol[18] and the behavior for large Z has been built into several recent non-empirical approximations (SCAN[19], APBE[20], acGGA[11]).

However, the simple powers of $Z^{1/3}$ used in the original works[12, 13] were based on the scaling behavior of the gradient expansion itself. Here we provide three lines of evidence for the existence of a $Z\ln Z$ contribution for atoms. Thus the analytic forms used as 'exact conditions' are likely incorrect, and should be replaced by the new forms and coefficients suggested below.

This preliminary report summarizes the most important results of an on-going exploration. The first line of inquiry consists of evaluating the beyond-LDA exchange energy,

$$\Delta E_{\rm x} = E_{\rm x} - E_{\rm x}^{\rm LDA}\,, \tag{1}$$

for neutral atoms up to $Z = 120$, using the optimized effective potential (OEP). These data are plotted as $\Delta E_{\rm x}/Z$ versus $\ln Z$ in Fig. 1, and tend to a straight line if a $Z\ln Z$ term is the leading term. As can be seen, the data indeed lines up remarkably well with a logarithmic trend, giving a significantly better fit than that of Ref. [13]. A quantitative statistical analysis of different fits is given below.

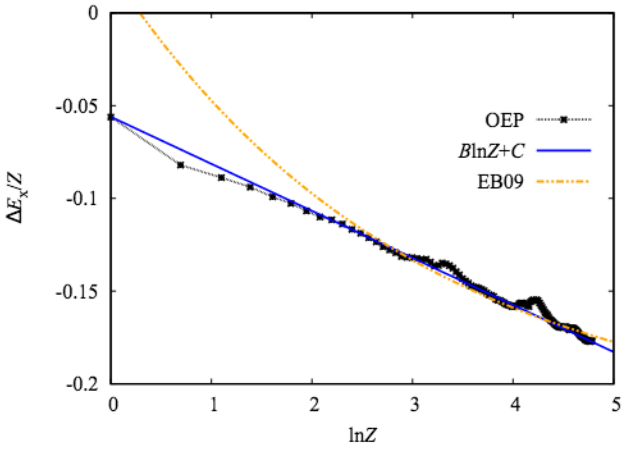

FIG. 1. Beyond-LDA exchange energy ($E_{\rm x} - E_{\rm x}^{\rm LDA}$) per electron of neutral atoms. The solid blue line is the new $B\ln Z + C$ fit described in the text, whereas the orange dashed curve is the fit of Ref. [13]. (Hartree atomic units used throughout.)

The second direction involves an analytic derivation of the logarithmic term, based on applying the GEA to the TF density profile for an atom.[21] It arises from the divergence of the gradient of the electron density in the inner region of a large atom, which is cut off and tamed in an appropriate manner. The coefficient of the $Z\ln Z$ term thus obtained is less than half the slope of the fit in Fig. 1, reflecting the aforementioned discrepancy with GGAs.

The third direction is a study of the Bohr atom[22], in which electron repulsion is effectively turned off by multiplying the interaction term in the Hamiltonian by an infinitesimal. In this case, the orbitals are hydrogenic and exchange energies were calculated analytically for atoms with up to 22 closed shells (7590 non-interacting electrons[23]), yielding coefficients of the Z expansion to many digits. The Bohr-atom LDA exchange energies were similarly evaluated and fit (this calculation is simpler, and was performed for up to 100 closed shells). Subtraction gives a $Z\ln Z$ term with a coefficient larger than that of neutral, interacting-electron atoms. Application of the GEA to this system reveals why this happens: in addition to the divergence in the inner region, where the attractive nuclear potential is dominant and electron repulsion is negligible, there is a further $Z\ln Z$ contribution from the cusp at the critical outer turning point where the Bohr-atom TF density abruptly vanishes. This is quantitatively equal to 1/3 of the inner-region contribution.

Overall, the $Z\ln Z$ coefficient for the Bohr atom is 2.7 times larger than that of the gradient expansion for that system. Assuming that for all atoms the $Z\ln Z$ coefficient is precisely 2.7 times larger than its GEA value yields analytic values for the Bohr atom, neutral atoms, and any partially-ionized atom, in good agreement with the data of Fig. 1.

Our first step is a detailed analysis of the numbers in Fig. 1. The goal here is to discern, via numerical considerations only, the leading term in the correction to the LDA exchange energy, and to find its coefficient. Three candidates for the leading correction are: a term proportional to Z from scaling considerations [13]; the $Z\ln Z$ dependence suggested by the gradient expansion discussed below; and finally, a term proportional to $Z^{4/3}$, motivated by the existence of such a term in the total energy, describing the growth in the amplitude of oscillations across the periodic table.[24] The general form

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

enables a discussion of all these possibilities.

To acquire the data set for Fig. 1, we use the OPMKS code [25] to calculate $E_{\rm x}$ with the optimized effective potential for non-relativistic neutral atoms up to $Z = 120$, extending an earlier data set[10]. Unfortunately, the inversion to find the OEP potential fails for larger Z. LDA data are obtained using the OPMKS code, and extended for closed-shell atoms up to $Z = 978$ (with $17s^2$ valence shell) using the FHI98PP pseudopotential code [26], run in its all-electron mode. In contrast to the OPMKS results, correlation effects are included in the LDA calculations, but for large-Z atoms the effects on the exchange energy are insignificant.

	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	-0.006(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), in mHa, 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.

To obtain a data set suitable for statistical analysis, we remove the large numbers of highly correlated data points across subshells, keeping only atoms with closed subshells: the alkaline earths (closed s shell), noble gases (p shell), group 12 metals (d shell), and closed f-shell atoms. This avoids bias towards wider rows of the periodic table. There are 20 such atoms for $Z \leq 120$, but we opt for an $n = 16$ atom set, excluding the first instance of each series ($Z = 2$, 10, 30, and 70), as these represent a point of maximum deviation from the trend followed by the majority of atoms[10] due to oscillations in Z.

To generate a set of competing models for our data, we select a subset of coefficients in Eq. (2) to vary, 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.

The first (and worst) two forms are those where the constant term is the leading order contribution to $\Delta E_{\rm x}$, including the form finally assumed in Ref. [13]. The third line, which adds a $Z\ln Z$ contribution, has the smallest errors in coefficients and the best $\chi_{\rm red}$, implying an rms deviation from the fit of less than 1 mHa. Moreover, this type of fit does remarkably well also *outside* the range of Z for which the fit was optimized, even down to hydrogen, as seen in Fig. 1.

The remaining fits test possibilities with additional free parameters. The most likely missing term would be a $Z^{1/3}$ term, which we have added in fits 5 and 7. This slightly degrades the fit, as $\chi_{\rm red}$ increases ($n - m$ decreases more than $\sum_i \delta_i^2$), and the standard error for A' is significantly greater than the value of the term itself, suggesting it should be set to zero, as in Ref. [13]. Adding a term proportional

to $Z^{-1/3}$ also worsens the fit, as seen in fits 4 and 7. Fit 6, using only powers of $Z^{1/3}$ without a logarithmic term, also results in a somewhat larger $\sum_i \delta_i^2$ despite the larger number of free parameters.

We carry out a further test to discriminate between the best of our models, model 3, with a ln$Z$ leading term and model 6, with $Z^{1/3}$. An asymptotic series should increase in accuracy as Z increases, so we refit our model to a more restricted set of data: first by dropping a second row for each filled-shell column, to keep 12 atoms, and then by dropping a third row, keeping 9 atoms. For the ln$Z$-leading model, the three fits yield essentially the same results, differing from each other by statistically marginal amounts. Using the 12 atom set starting at $Z = 12$, we find $B = 0.0254$ and $C = 0.0560$; for the 9 atom set, starting at $Z = 20$, we find $B = 0.0253$ and $C = 0.0562$, essentially unchanged from the 12-atom set but with slightly higher standard errors. For the $Z^{1/3}$ model, the coefficients drift noticeably as the data is restricted to a smaller range. The coefficient A goes from -12.8 for the 16 atom set, to -10.3 and -9.0 for the the 12- and 9-atom sets. The D coefficient drifts comparably. This behavior is consistent with the EB09 curve in Fig. 1 where the fit is tailored to the range of data being fit and fails outside it. In other words, although any number of models can be fit to the data over a limited range (given sufficiently many free parameters), those incorporating the ln$Z$ term are clearly the most predictive.

Overall, for a best judgement of the asymptotic expression for our data, we take the ln$Z$ model weighted as much as possible to large Z without penalty in standard error, yielding

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

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. This provides yet another example of "the principle of unreasonable utility of asymptotic estimates," elicited by Schwinger in the context of the semiclassical expansion for the overall energy of atoms [28].

The next step aims for a theoretical prediction of the leading correction to the LDA exchange energy. Leading terms can often be derived directly from the asymptotically accurate TF approximation, with no need for explicit solutions to the electronic problem. For example, the LDA exchange energy is given by

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

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 to exchange as $Z \to \infty$,

$$E^{\rm TF} = -A\, Z^{5/3}, \qquad (5)$$

where $A \approx 0.2208274$ (see [10]).

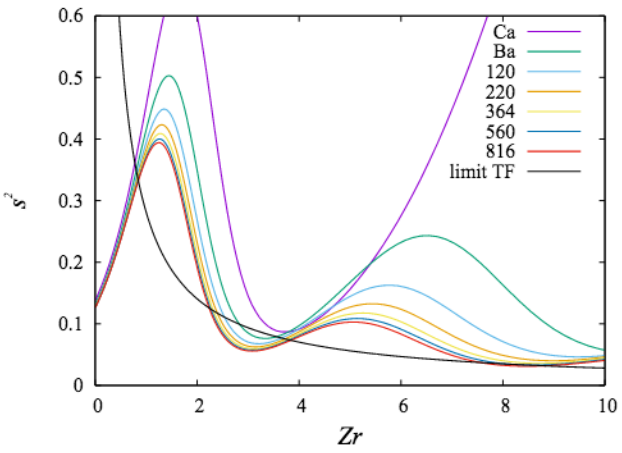

FIG. 2. Plot of s^2 near the nucleus versus distance, scaled as Zr, for alkaline earth atoms ranging from Ca up to $Z = 816$ which has valence shell $16s^2$. The black line shows the TF model.

For the beyond-LDA contribution to the exchange energy, Eq. (1), it makes sense to try the gradient expansion approximation of DFT[17, 29], despite the discrepancy with exact results mentioned above. The leading correction to LDA is given in this approach by

$$\Delta E_{\rm x}^{\rm GEA} = -\mu^{\rm GE} a_{\rm x} \int n^{4/3}(\mathbf{r})\, s^2(\mathbf{r})\, d^3r \qquad (6)$$

where $s = |\nabla n|/(2k_{\rm F}n)$ is the dimensionless gradient parameter and $k_{\rm F} = (3\pi^2)^{1/3} n^{1/3}$ is the local Fermi wavenumber. The coefficient $\mu^{\rm GE}$ was deduced to have the value of 10/81 by applying perturbation theory to a uniform electron system.[30] Application of Eq. (6) to the slowly-varying gas yields a term of order Z when scaled toward the TF limit[12] via $n_Z(r) = Z^2 n(Z^{1/3}r)$.

As gradients are weak in the bulk of large atoms, with s of order $Z^{-1/3}$, it is natural to evaluate $\Delta E_{\rm x}^{\rm GEA}$ to leading order using the TF profile, but this requires care. 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

$$n^{\rm TF}(r) \simeq \frac{1}{3\pi^2}\left(\frac{2Z}{r}\right)^{3/2}, \qquad r \ll Z^{-1/3}\,, \qquad (7)$$

which has

$$s^{\rm TF}(r) \simeq \frac{3}{4}\frac{1}{\sqrt{2Zr}}\,, \qquad r \ll Z^{-1/3} \qquad (8)$$

as its gradient. This approximation fails in the region where the inner shell (1s) electrons dominate, as illustrated in Fig. 2, which shows s^2 of alkaline earths up to $Z = 816$ and of the TF density, Eq. (8), as a function of Zr. 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 $r = 1/Z$. Working out the various factors in Eq. (6) and keeping only the divergent contribution gives:

$$\Delta E_{\rm x}^{\rm GEA} \simeq -\frac{9\mu^{\rm GE}}{8\pi^2} Z \int_{Z^{-1}}^{Z^{1/3}} \frac{dr}{r} , \qquad (9)$$

which yields a logarithmic term,

$$\Delta E_{\rm x}^{\rm GEA} = -\frac{3\mu^{\rm GE}}{4\pi^2} Z\ln Z + O(Z) . \qquad (10)$$

The second term on the right accounts for the non-divergent contributions from the regions near and beyond the limits of integration in Eq. (9). We define

$$B = -\lim_{Z\to\infty} \Delta E_{\rm x}/(Z\ln Z) , \qquad (11)$$

and our derivation yields

$$B^{\rm GEA} = \frac{3}{4\pi^2}\mu^{\rm GE} \qquad (12)$$

or about 9.38 mHa. The presence of such a logarithmic term in the GEA for atoms was very recently noticed in [31], and could be inferred from earlier work (see Appendix A of [11]).

We have no rational for the difference between the results of the GEA, Eq. (12), and the actual data, Eq. (3), i.e., the slope in Fig. 1. The GEA coefficient is too small by a factor of about 2.7. One might suspect that it may be altered by a known redefinition of the GEA involving integration by parts [32], but checking this reveals that Eq. (12) is unaffected (unlike, e.g., the 4th order contribution to the kinetic energy of atoms[33]).

So far, we have shown that the beyond-LDA exchange energy of large-Z atoms has a leading $Z\ln Z$ term for both numerical exchange data and the GEA, but the two results do not agree quantitatively. In order to shed further light on the matter, we turn to the Bohr atom, whose relative simplicity (hydrogenic orbitals) allows more precise 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. (The Bohr atom also corresponds to the limit of highly ionized atoms, $N << Z$, where N is the number of effectively non-interacting electrons[34].)

The exchange energy of this system, defined by an infinitesimal Coulomb repulsion, was evaluated analytically for values of N corresponding to up to 22 completely full electron shells ($N = 7590$), with Slater exchange integrals[35] expressing the exchange energy for the electrons of any pair of subshells (using Mathematica). Our extremely accurate fit has the form

$$E_{\rm x}^{\rm Bohr}(N) = \qquad (13)$$
$$-A_o N^{5/3} - (\bar{B}_o \ln N + \bar{C}_o)N - (\bar{D}_o \ln N + \bar{E}_o)N^{1/3} + .. ,$$

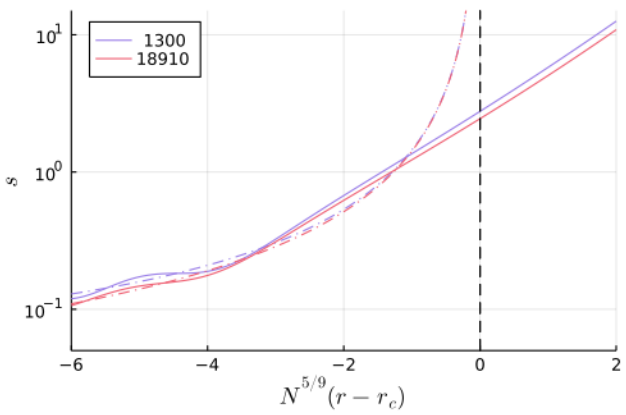

FIG. 3. Plot of the gradient parameter s near the edge of the Bohr atom, versus distance from the cutoff radius scaled by $N^{5/9}$, for two representative values of N identified in the legend. Dot-dashed lines: the results of the corresponding TF models, which diverge at r_c (dashed vertical line).

where the subscript denotes a Bohr-atom coefficient and the bar denotes the exchange energy itself. The leading coefficient is $(2/3)^{1/3}(4/\pi^2)$, from LDA applied to the TF density[34]. Subtracting this from $E_{\rm x}^{\rm Bohr}$ and fitting the remainder yields a value of $\bar{B}_o$ that agrees with $7/(27\pi^2)$ to 5 digits. Taking the analytic number and subtracting it off, yields $\bar{C}_o = 45.3536$, $\bar{D}_o = -3.17$ and $\bar{E}_o = 0.6$, in mHa, determined to the number of digits shown. The fact that each pair of terms is significantly smaller than the preceding terms attests to the efficiency of the expansion and is of great assistance in performing the fit.

We repeat the procedure for LDA evaluated on Bohr-atom (hydrogenic) densities. In this case, there are also $O(N^{2/3}\ln N)$ and $O(N^{2/3})$ terms, and the results are 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 ($N = 676700$). We find $\bar{B}_o^{\rm LDA}$ to match $-2/(27\pi^2)$ to within $\sim 0.1\%$ (note the opposite sign), with increasing accuracy for larger N, yielding

$$B_o = \bar{B}_o - \bar{B}_o^{\rm LDA} = \frac{1}{3\pi^2} . \qquad (14)$$

The fact that the result is significantly larger than that for neutral atoms, Eq. (3), may appear surprising at first, but this is resolved by looking at the GEA for this system, to which we turn next.

In order to apply the GEA, Eq. (6), to the Bohr atom, we again turn to its TF density distribution:

$$n_o^{\rm TF} = \frac{(2N)^{3/2}}{3\pi^2}\left(r^{-1} - r_c^{-1}\right)^{3/2} , \qquad r \le r_c , \qquad (15)$$

where $r_c = (18/N)^{1/3}$ is a sharp cutoff radius beyond which the density vanishes, $n_o^{\rm TF} = 0$ (see the second appendix of [34] for details). The corresponding dimensionless gradient

s diverges not only as r approaches 0, precisely as in Eq. (8), but also as r approaches r_c [34], as

$$s_o \simeq \frac{3}{4}\frac{3^{2/3}}{2^{1/6}}\left[N^{5/9}(r_c - r)\right]^{-3/2}, \quad 0 < r_c - r \ll N^{-1/3}. \tag{16}$$

The result is

$$\Delta E_o^{\rm GEA} \simeq -\frac{9\mu^{\rm GE}}{8\pi^2} N \left[\int_{N^{-1}}^{N^{-1/3}} \frac{dr}{r} + \int_0^{r_c - N^{-5/9}} \frac{dr}{r_c - r}\right], \tag{17}$$

where the first logarithmic divergence is treated as above, and 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 $N^{-5/9}$,[36] as displayed in Fig. 3. As a result, the contribution of the second divergence is 3 times smaller than that of the first (again regardless of integration by parts). The GEA thus yields a $Z\ln Z$ coefficient 4/3 times larger on the Bohr atom than its interacting neutral-atom counterpart, Eq. (12):

$$B_o^{\rm GEA} = \frac{\mu^{\rm GE}}{\pi^2}. \tag{18}$$

There are several noteworthy similarities and differences between the inner and the outer divergence. One similarity is that the cutoff of the integration kicks in just as the growth of s leads to values of order unity, as shown in the figure (it is of order $N^{-1/3}$ in the bulk of the density distribution). One difference is that whereas s for the actual density profile near the nucleus remains finite and reasonably small, near r_c one is entering the region of evanescent wavefunctions, and s begins to grow exponentially (see Fig. 3).

For the large values of s typical of evanescent regions, the GEA is expected to be very inaccurate, and it is standard in GGAs to replace s^2 in Eq. (6) by a factor which does not continue to grow with s. However, the fact that the density n also becomes very small in such regions limits the importance of this type of inaccuracy: the GEA integral, Eq. (6), remains finite, and the GGA reduction in the contribution from large values of s only affects the $O(Z)$ contribution to $\Delta E_{\rm x}$, leaving the $Z\ln Z$ term unchanged.

The two regions also determine $\bar{B}_o^{\rm LDA}$. The inner region of the density has been studied in detail in [22]. The leading non-oscillatory correction to the TF density profile yields $n(r) \simeq n^{\rm TF}(r)[1 - 1/(64Zr)]$ for $Z^{-1} \ll r \ll Z^{-1/3}$, producing a contribution of $-1/(18\pi^2)$ via Eq. (4). Consistency with the result $\bar{B}_o^{\rm LDA} = -2/(27\pi^2)$, Eq. (14), requires that the outer divergence yields a contribution 1/3 as large as the first, just as for $B_o^{\rm GEA}$.

To conclude the discussion of the Bohr atom, a comparison of the analytic GEA result with the direct evaluation is called for. One finds from Eq. (18) that $B_o^{\rm GEA} = \mu^{\rm GE}/\pi^2 = 10/(81\pi^2)$, using the standard coefficient. Thus, the value excogitated from the highly precise numerical results, Eq. (14), is exactly 27/10 times larger than that of the GEA. It is tempting to conjecture that

$$B = \frac{27}{10} B^{\rm GEA} \tag{19}$$

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. This is very close to our best numerical fit, Eq. (3).

Furthermore, this conjecture has implications for additional systems — highly ionized atoms, which for a constant N/Z ratio have a well-defined asymptotic expansion, based on a known solution to the TF equation. The inner region of such systems is essentially determined by the nuclear charge Z, very similar to that of the first logarithmic divergence above, whereas the remaining charge, $Z-N$, essentially determines the outer region. This gives the prediction

$$B = \frac{1}{12\pi^2}\left(4 - \frac{N}{Z}\right) \tag{20}$$

for the $Z\ln Z$ leading coefficient in the asymptotic expansion for the beyond-LDA exchange energy of such highly-ionized atoms, interpolating smoothly between the Bohr atom result and the neutral-atom conjecture.

Last, we turn to the implications for approximate functional development. Our derivation applies to most GGA's for the exchange energy, which are usually written in terms of an enhancement factor,

$$E_{\rm x}^{\rm GGA} = -a_{\rm x}\int n^{4/3}(\mathbf{r}) F_{\rm x}(s(\mathbf{r}))\, d^3r\,. \tag{21}$$

Typically, $F_{\rm x} \approx 1 + \mu^{\rm GGA} s^2 + \ldots$ for small s, and this regime of the enhancement factor is dominant in the TF limit. Thus Eq. (12) also applies to any such GGA, with $\mu^{\rm GE}$ replaced by $\mu^{\rm GGA}$. This yields 16.7 mHa for PBE and 20.9 mHa for B88 for the coefficient of the $Z\ln Z$ term (see [13] for a detailed discussion of these approximations). If compared to the GEA, these are substantially closer to the value of 25.4 mH of Eq. (3), but not as close as expected based on the fact that both yield accurate exchange energies for atoms for Z between 10 and 100. Evidently, this is 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, will be accurate for all practical calculations, but in the future both the $\ln Z$ terms and higher order corrections should be studied separately.

In fact, combining our conjecture with the data for the hydrogen atom, used as a 'norm'[19], yields:

$$\Delta E_{\rm x}^{\rm normed} = -Z\left\{\frac{\ln Z}{4\pi^2} + \frac{5}{16} - 0.2564\right\}, \tag{22}$$

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. (Of course, calculations of real high-Z atoms and materials must include relativistic corrections, but such corrections cannot be usefully compared with empirical data if the underlying non-relativistic calculation is worsening with increasing Z.) Further research is necessary for such improvements to be achieved.

One research direction would involve a study of 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 [many simplifications, e.g., dropping the self-consistency loop typical of DFT calculations and using instead the potential of the TF solution as an effective potential, are not expected to alter the $O(Z\ln Z)$ and $O(Z)$ terms]. 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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