Non-empirical derivation of the parameter in the B88 exchange functional

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Abstract: The B88 exchange energy density functional (created by Becke in 1988) is a crucial part of the most popular density functional in use today, B3LYP. B88 contains one empirical parameter which was fitted to Hartree–Fock exchange energies for the noble gas atoms. We show how local approximations to exchange become relatively exact under a very specific approach to the limit of large numbers, but the usual gradient expansion does not. The leading corrections can be captured by generalized gradient approximations, producing a non-empirical derivation of the parameter in B88.

Key words: density functional theory (DFT), exchange functional, B88, potential scaling.

Résumé : La fonctionnelle de la densité d'énergie d'échange B88 (développée par Becke en 1988) est une partie cruciale de la fonctionnelle de densité B3LYP, la plus populaire parmi les bases en usage aujourd'hui. La fonction B88 comprend un paramètre empirique qui a été ajusté aux énergies d'échange d'Hartree–Fock des atomes des gaz rares. On démontre comment des approximations locales des échanges deviennent relativement exactes dans une approche très spécifique à la limite des grands nombres, ce que l'expansion habituelle des gradients ne permet pas. Les corrections principales peuvent être capturées par les approximations de gradients généralisées et produire une dérivation non empirique du paramètre dans la fonction B88.

Mots-clés : théorie de la fonctionnelle de densité (TFD), fonctionnelle d'échange, B88, mise à l'échelle du potentiel.

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I. Introduction

Density functional theory (DFT) has become the method of choice for many electronic structure calculations in quantum chemistry.[1] It balances the demands of accuracy and computation time, making it advantageous to other available methods. Although DFT is a formally rigorous theory, in practice, it requires an approximation to the exchange-correlation (XC) energy, E_{xc}, as a functional of the density. In the late 1980s and early 1990s, approximations, such as B88, were developed which proved accurate enough for their application in many areas of both chemistry and physics. The explosion in the use of DFT, driven by newly available computational power, could not have succeeded without the development of such functionals.

Modern DFT began with the Hohenberg–Kohn theorem of 1964[2] and the Kohn–Sham scheme of 1965.[3] The first approximation to the XC energy was the local density approximation (LDA), which uses only the density at a given point to determine the energy density at that point. This is exact for a uniform gas, since it is the known energy density of the uniform gas that is used to define LDA. The natural successor to LDA is a semi-local (or gradient-corrected) approximation which adds information about the derivative of the density at that point. In fact, in the same paper in which LDA is introduced, so too is the gradient expansion approximation (GEA) for XC. The coefficients of the GEA are determined by the energy of a slowly varying gas.[4–6] However, it was found that the GEA often worsened LDA results, and two decades passed before substantial improvements were made.

Generalized gradient approximations (GGAs) effectively resum the gradient expansion, but using only $|\nabla n|$. The B88 functional[7] is the most used GGA for exchange overall (as part of B3LYP[8,9]), but the most popular GGA in solid-state applications is PBE.[10] Neither reduces to the GEA in the limit of small gradients. In this paper, we explain the reason why this must be the case. Asymptotic expressions for the energy components as functionals of N, the number of electrons, display "unreasonable accuracy"[11] even for low N. To give good energies for finite systems, any approximate XC functional must have accurate coefficients in its large-N expansion. LDA gives the dominant contribution, but the GEA does not yield an accurate leading correction for atoms. Popular GGAs such as B88 and PBE do get this correction right.

In ref. 12, the underlying ideas behind this work were developed; however, the reasoning was based upon scaling the density and not on the potential scaling discussed below. We refine these ideas and explicitly show how they can be used for functional development, and in particular, we show how the parameter in B88 may be derived in a non-empirical manner.

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II. Background theory

In this section, we review the theory behind asymptotic expansions of the energy, including the expression for the exchange energy. A demonstration of the usefulness of this asymptotic expansion for exchange is also given, where the constant in LDA is found without referring to the electron gas. We also show the form of the gradient correction to LDA exchange, as well as discussing the form of the GGAs, B88, and PBE.

A. Asymptotic expansion in N

Begin with any system (atom, molecule, cluster, or solid) containing N electrons. We then imagine changing the number of electrons to N'. Since we usually begin from a neutral system, usually we consider only $N' > N$. Thus, we define a scaling parameter $\zeta = N'/N > 1$. As we change the particle number, we simultaneously change the one-body potential $v_{ext}(\mathbf{r})$ in such a way as to retain overall charge neutrality, which means

$$[1] \qquad v_{ext}^{\zeta}(\mathbf{r}) = \zeta^{4/3} v_{ext}(\zeta^{1/3}\mathbf{r}), \qquad N \rightarrow \zeta N$$

We refer to this as charge–neutral (CN) scaling. For an isolated atom, $Z \rightarrow \zeta Z$ under this scaling, so it remains neutral as the electron number grows. For molecules with nuclear positions R_α and charges Z_α, $Z_\alpha \rightarrow \zeta Z_\alpha$, and $R_\alpha \rightarrow \zeta^{-1/3} R_\alpha$. In the special case of neutral atoms, the resulting series for the energy is well-known:

$$[2] \qquad E = -a_0 N^{7/3} - a_1 N^2 - a_2 N^{5/3} - \dots$$

where $a_0 = 0.768745$, $a_1 = -1/2$, and $a_2 = 0.269900$.[11,13] We say an approximation is large-N *asymptotically exact* to the pth degree (AEp) if it recovers exactly the first $p + 1$ coefficients for a given quantity under the potential scaling of eq. [1]. Lieb and Simon[14,15] showed that Thomas–Fermi (TF) theory becomes *exact* in the limit $\zeta \rightarrow \infty$ for *all* systems. TF is exact in a statistical sense, in that TF gives the correct first term of eq. [2], but not the other terms. We say TF is AE0 for the total energy.

A similar expression exists for the exchange component of the energy alone

$$[3] \qquad E_x = -c_0 N^{5/3} - c_1 N - \dots$$

where $c_0 = 0.2208 = 9a_2/11$, and c_1 will be the main topic of this paper. In a similar fashion, Schwinger demonstrated that the local approximation for exchange is AE0, and this coefficient is given exactly by local exchange evaluated on the TF density.[11,13,16] However, to give atomic exchange energies needed for chemical accuracy, any exchange approximation should be at least AE1.

Now, suppose we want to make a local approximation for E_x but know nothing about the uniform gas. Dimensional analysis (coordinate scaling[17]) tells us that it must be of the form:

$$[4] \qquad E_x^{LDA}[n] = A_x I, \quad I = \int \mathrm{d}^3 r n^{4/3}(\mathbf{r})$$

Requiring that this gives the leading contribution to eq. [3] then fixes the value of the constant A_x. Using any

(all-electron) Hartree–Fock atomic code, such as were already available in the 1960s,[18] one calculates I for densities running down a particular column of the periodic table and then deduces its dependence on $Z^{5/3}$. A modern alternative is to use the fully numerical OPMKS code[19] using the OEP exact exchange functional to find densities for neutral atoms from $Z = 1$ to $Z = 88$. By fitting, one finds $I = 0.2965 Z^{5/3}$ and hence $A_x = -0.7446$. This is remarkably close to the derived result of

$$[5] \qquad A_x = -\frac{3}{4}\left[\frac{3}{\pi}\right]^{1/3} = -0.7386$$

Thus, without any recourse to the uniform electron gas, we have derived the correct local approximation to $E_x[n]$. This demonstrates that, via asymptotic exactness, the local approximation to exchange is a universal feature of all systems as $N \rightarrow \infty$, when scaled appropriately. (In fact, Schwinger only proved this for atoms,[11] we know of no proof for arbitrary systems).

B. Gradient expansions

The next step up the ladder of increasingly sophisticated density-functional approximations[20] is a semi-local approximation for $E_x[n]$, i.e., one which includes information about the gradient of the density. We introduce the dimensionless measure of the gradient:

$$[6] \qquad s(\mathbf{r}) = \frac{|\nabla n(\mathbf{r})|}{2k_F(\mathbf{r})n(\mathbf{r})}$$

where $k_F(\mathbf{r}) = (3\pi^2 n(\mathbf{r}))^{1/3}$ is the local Fermi wave vector. This is often written in terms of $x = |\nabla n|/n^{4/3}$, which is simply proportional to s. Assuming smoothness in s and no preferred spatial direction, we know any sensible approximation depends only on s^2. The gradient expansion is defined as the expansion of the energy as a functional of the density around the uniform limit. The leading correction for exchange is

$$[7] \qquad E_x^{(2)}[n] = \mu \int \mathrm{d}^3 r s^2(\mathbf{r})\epsilon_x^{LDA}(n(\mathbf{r}))$$

where $\epsilon_x = A_x n^{4/3}$ and μ is a constant. Alternatively, we may write

$$[8] \qquad E_x^{(2)}[n] = -\beta \int \mathrm{d}^3 r n^{4/3}(\mathbf{r}) x^2$$

with

$$[9] \qquad \beta = \frac{3}{16\pi}\left[\frac{1}{3\pi^2}\right]^{1/3}\mu$$

In a very slowly-varying electron gas, the gradient is very small, and the exchange energy will be accurately given by $E_x^{LDA} + E_x^{(2)}$. For such systems, the constant $\mu = 10/81$,[4] so that $\beta \approx 0.0024$.

The gradient expansion approximation (GEA) means applying this form to a finite system, using the value of μ from the slowly-varying gas. The GEA for exchange typically reduces the LDA error by about 50%. However, it's counterpart for correlation worsens the LDA error, as its en-

ergy density is not even always negative. In many cases, GEA strongly overcorrects LDA leading to positive correlation energies and giving poor total energies.[5]

A generalized gradient approximation (GGA) seeks to include the information contained in $s(\mathbf{r})$ while improving on the success of LDA. The B88 exchange functional was designed to reduce to the GEA form when s is small, but also recover the correct $-n(r)/2r$ decay of the exchange energy density for large r in atoms. Thus, it interpolates between two known limits, and has the form:

$$[10] \quad \Delta E_x^{B88}[n] = -\beta^{B88} \int d^3r\, n^{4/3}(\mathbf{r}) \frac{x^2}{1 + 6x\beta^{B88}\sinh^{-1}[2^{1/3}x]}$$

where ΔE_x denotes the correction to LDA. Thus, the B88 functional[7] contains one unknown parameter, β^{B88}. In 1988, Becke found this parameter by fitting to the Hartree–Fock exchange energies of the noble gases, finding a value of 0.0053. In fact, Becke notes that this value is consistent with the observation of a high-Z asymptote for β. In ref. 21, B86, Becke calculates what value of β in eq. [8] is required to give the HF exchange energy for each atom in the first two rows of the periodic table along with the noble gas atoms. Thus, β is treated as a function of Z, and he observes that it converges for high-Z. Thanks to the previous section on asymptotic series, we can now understand why this convergence occurs. Although the B88 form reduces to that of the gradient expansion for small gradients, the value for β is about twice as large as that predicted from the slowly varying gas.

Another common GGA for exchange is the Perdew–Burke–Ernzerhof (PBE) approximation,[10] usually written in terms of an enhancement factor, $F_x(s)$, to the LDA exchange energy density

$$[11] \quad E_x^{PBE}[n] = \int d^3r\, F_x^{PBE}(s)\epsilon_x^{LDA}[n]$$

where

$$[12] \quad F_x^{PBE}(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2/\kappa'}$$

and $\mu = 0.2195$ and $\kappa = 0.8040$. This form for the enhancement factor is chosen so that it reduces to LDA for $s = 0$ and again recovers the form of the gradient expansion for small s. For large s, it becomes a constant determined by the parameter κ. Both κ and μ are determined via satisfaction of various exact conditions. The value of μ was chosen to preserve the good linear response of LDA for the uniform electron gas under a weak perturbation,[22,23] while κ is set by the Lieb–Oxford bound[24] on the exchange-correlation energy. (That condition is obviously violated by B88, while PBE does not accurately recover the X energy density in the tails of Coulombic systems).

III. Theory

LDA yields the dominant term in *either* the asymptotic charge–neutral expansion ($\zeta \to \infty$) *or* the gradient expansion for the slowly varying electron gas, $s \to 0$. We next show that, contrary to popular myth, the important expansion is the charge–neutral expansion, *not* the gradient expansion.

The charge–neutral expansion can be applied to any type of matter, be it molecule or extended solid. For any finite system, the density decays exponentially far from the nuclei. This is a key distinction between finite systems and bulk matter, treated with periodic boundary conditions. Bulk matter has no such regions.

But, for slowly varying gases, or more generally when there are no classical turning points at the Fermi surface, the charge–neutral scaling and the gradient expansion become identical, i.e., the gradient expansion for the slowly varying gas is simply a *special case* of charge–neutral scaling. To see that this is so, consider just the kinetic energy as a density-functional. Here, the gradient expansion is known out to 6th order,[25] and eventually, the integrated quantity itself diverges for atomic densities due to the evanescent tail. But no such divergence occurs for extended systems with finite density everywhere.[25,26]

Thus, CN scaling applies to all systems, but only becomes identical to the gradient expansion for slowly varying bulk systems. For the dominant contribution, effectively the local Fermi wavelength becomes short on the length scale on which the density is changing, so that the local approximation applies and yields the exact answer for this term. Hence, LDA reproduces the AE0 terms, but GEA does *not* produce the leading corrections. All this has been amply demonstrated for simple 1D model systems[16] and for the Kohn–Sham kinetic energy for atoms.[27]

Here, we apply the same reasoning for exchange. The local approximation becomes relatively exact as $\zeta \to \infty$, but the gradient expansion does not reproduce the leading correction in the CN expansion. Below, we use the simple reasoning of ref. 12 to recover this leading correction. We perform a much more extensive calculation of the asymptotic behavior, using methods developed in ref. 27. We find, in agreement with ref. 12, that the leading correction for atoms is about double that given by the gradient expansion, matching quite closely that of B88 and of PBE. Reversing this logic for B88, we show that B88 may be more or less derived non-empirically via the constraint that the approximation be AE1. If we enforce AE1 exactly, we find a slightly different value for β, and discuss the properties of the resulting functional, excogitated B88.

IV. Extracting asymptotic coefficients

Under the potential scaling of eq. [1], any approximation for the exchange energy that reduces to LDA in the uniform limit has an expansion in N like eq. [3], with the same value for c_0. However, the coefficient c_1 depends on the particular approximation. Below, we explain the procedure used to extract these coefficients.

As mentioned in the previous section, the OPMKS[19] electronic structure code is a fully numerical electronic structure code that has the ability to perform optimized effective potential (OEP) calculations. We evaluate the various approximations using atomic densities found with the OEP exact exchange (EXX) method. The densities found using this method will be extremely close to the exact densities despite the fact that correlation is missing. Moreover, the effect of correlation will contribute at higher orders in the asymptotic expansions of the energy than those we are interested in.

Fig. 1. The OEP exact exchange energies E_x for neutral atoms from $Z = 1$ to 88, divided by $Z^{5/3}$ to pick out the leading term in its asymptotic series. The leading corrections are proportional to powers of $Z^{-1/3}$. The values for the noble gas atoms are given as the circle symbols.
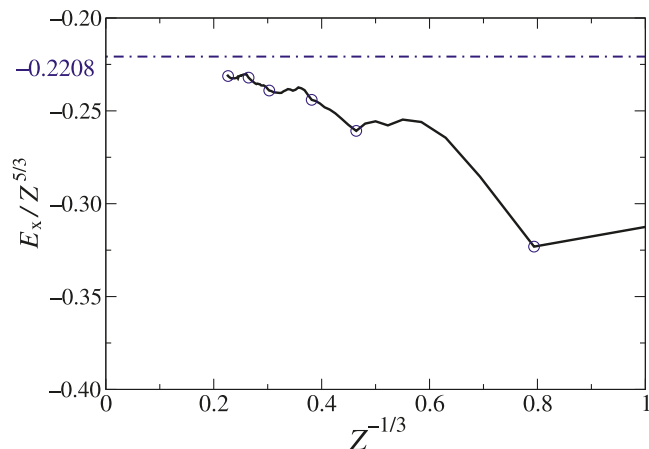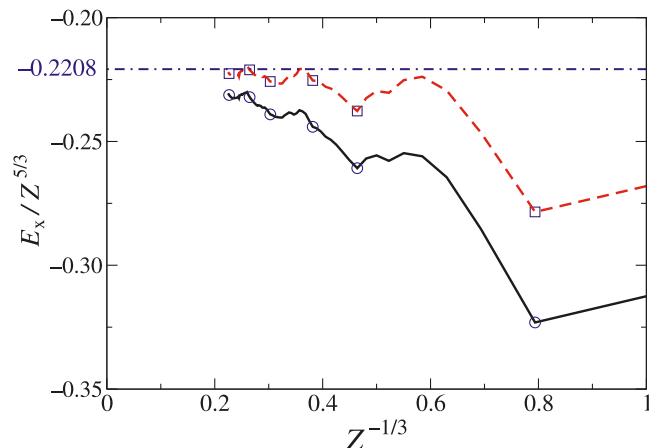

Fig. 2. We add to Fig. 1 the results for the LDA functional evaluated on the OEP densities (dashed-line) keeping the EXX values (solid line). As in Fig. 1, the noble gas atoms are highlighted with circle and square symbols for EXX and LDA, respectively.


Thus, EXX calculations are in principle sufficient for extracting the coefficient we seek.

In Fig. 1, we plot $E_x/Z^{5/3}$ vs. $Z^{-1/3}$ where E_x is the exchange energy from the exact exchange calculation. Since the leading term in the asymptotic expansion of eq. [3] is $Z^{5/3}$, this procedure picks out the c_0 coefficient as a constant while all other terms are functions of $Z^{-1/3}$. One can see that the curve in Fig. 1 is heading towards the exact value of $c_0 = -0.2208$, but it is difficult to extract higher coefficients due to oscillation of the curve due to the shell structure.

To overcome this difficulty, in Fig. 2, we add the LDA curve to Fig. 1. It can be seen that it too recovers the exact c_0 coefficient, but also clearly differs in higher orders in the asymptotic expansion. More usefully, we see that the LDA curve mimics the oscillations shown by exact exchange, so subtracting LDA from EXX will minimize this effect and make the extraction of asymptotic coefficients more accurate.

In Fig. 3, we plot $(E_x - E_x^{LDA})/Z$ vs. $Z^{-1/3}$ and find that it behaves close to linearly. There appears to be no $Z^{4/3}$ term

Fig. 3. We now find the next coefficient in the exchange asymptotic series. To minimize the error due to shell structure oscillations, the LDA exchange energy is subtracted from the exact exchange for each atom. As both give the leading correction, their difference will then have $\Delta c Z$, $\Delta c = c_1 - c_1^{LDA}$, as the leading term in its asymptotic expansion. The dashed line is the result of fitting to the noble gas atoms (circle symbols).
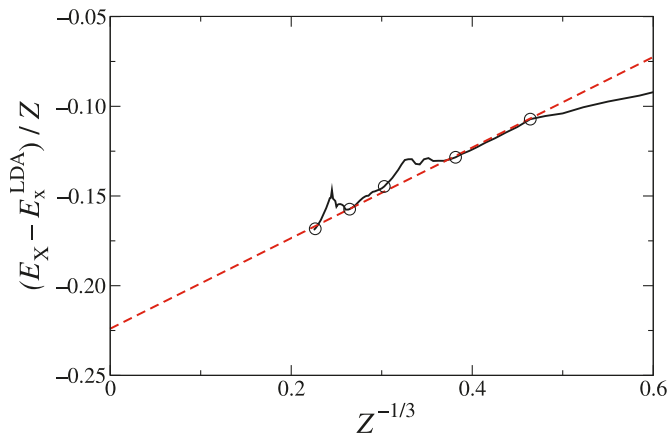
in E_x. Such a contribution was argued not to exist in ref. 12, but this was based on CN scaling of the density and studying the behavior of the terms in the gradient expansion. That reasoning is insufficient, as the expansion should be performed in terms of the potential, as described in section II. But since the Scott correction (the Z^2 contribution to the total energy) comes from the core region, there is no reason to expect an analogous contribution for exchange. To show this and also to precisely determine the c_1 coefficient, one should use the techniques developed by Schwinger for deriving the Scott correction to the total energy,[11] but apply them to exchange.

To further reduce the remaining uncertainty due to shell structure oscillations, we choose simply to use the noble gas atoms (excluding helium) for our fit. The strongest deviations from linearity come from the transition metals and lanthanides and actinides. We fit the difference $(E_x - E_x^{LDA})/Z$ with a straight line in $Z^{-1/3}$, and extrapolate to $Z \to \infty$, finding $\Delta c = -0.2240$, where $\Delta c = c_1 - c_1^{LDA}$, and
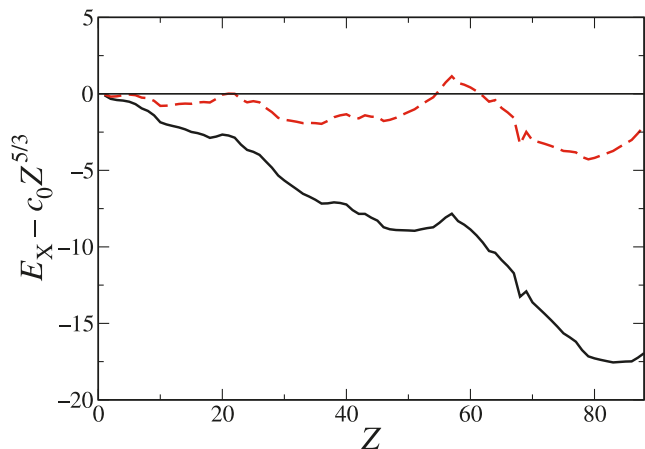
$$[13] \qquad E_x \approx E_x^{LDA} - 0.2240\, Z + 0.2467\, Z^{2/3}$$

The coefficient of the last term is given by the slope of the dashed line in Fig. 3, although the meaning of this term is unclear in the presence of such strong oscillating contributions.

If instead we used the alkaline earth atoms (excluding beryllium), we find an almost identical value, $\Delta c = -0.2236$. If we use all elements with $Z > 10$, we find a similar value, $\Delta c = -0.2164$. If all elements from $Z = 1$ to 88 are used, we find $\Delta c = -0.1982$. In ref. 12, Δc was found using noble gas atoms, except with the helium value included, and that method gave a value of $\Delta c = -0.1978$. In our analysis, atoms with $Z < 10$ are not used as they are not necessarily dominated by the asymptotic series.

Since LDA displays the shell oscillations that prevented us from fitting EXX directly, the value of the LDA c_1 coefficient cannot be found exactly. But we estimate

Fig. 4. To see that LDA does not significantly contribute to the higher orders of the exchange asymptotic series, we plot the difference between LDA and the leading term $c_0 Z^{5/3}$ (dashed line), as a function of Z. The exact exchange value is also shown (solid line).

Fig. 5. We use the same procedure as in Fig. 3 to find the Δc coefficient for the gradient correction to LDA, $E_x^{(2)}[n]$, as defined in eq. [7]. The dashed line was fitted to the noble gas atoms (circle symbols).


$0 \geq c_1^{\mathrm{LDA}} \geq -0.04$, i.e., at least five times smaller in magnitude than Δc. In Fig. 4, we show $E_x - c_0 Z^{5/3}$ as a function of Z for both the exact values and within LDA, demonstrating that the linear contribution comes almost entirely from the beyond-LDA terms.

Finally, we determine Δc for GEA. In Fig. 5, we plot $(E_x^{\mathrm{GEA}} - E_x^{\mathrm{LDA}})/Z$ vs. $Z^{-1/3}$ to find $\Delta c = c_1^{\mathrm{GEA}} - c_1^{\mathrm{LDA}}$, finding $\Delta c = -0.1062$. This plot is much closer to linear than the previous one. The leading corrections to LDA in the asymptotic expansion produce corrections to the shell structure *beyond* those captured by LDA evaluated on the exact density.[16,27] Although the smooth contribution can be partially captured by GEA, there is almost no correction to the shell structure. Just as for the kinetic energy,[27] GEA yields a correction to the smooth part that is about half of the accurate value.

To understand the power of these asymptotic expansions, we add the corrections of eq. [13] to the LDA energies, and in Fig. 6, plot the percentage error relative to exact exchange, as a function of Z. For all but the second row of the periodic table, the resulting error is below 0.5% in magnitude, and typically of the order 0.2%.

V. Generalized gradient approximations

Generalized gradient expansions were designed to improve energetics over LDA for electron systems of interest and relevance. Early versions, such as PW91,[28,29] were tortured into reducing to the gradient expansion when the density is slowly varying. But this was later given up, in both B88 and PBE exchange, which both reduce to the gradient expansion form for slow variations, but with coefficients much larger than that of the gradient expansion.

Our analysis explains why this must be so. Regardless of its derivation, any modern GGA for exchange is tested against the neutral atoms. Any approximation that cannot recover the right c_1 will be generally inaccurate for these energies, and so discarded. Thus, any that become popular have already passed this test.

In Table 1, we give the results for Δc for several different functionals. The same methodology was used in all extrac-
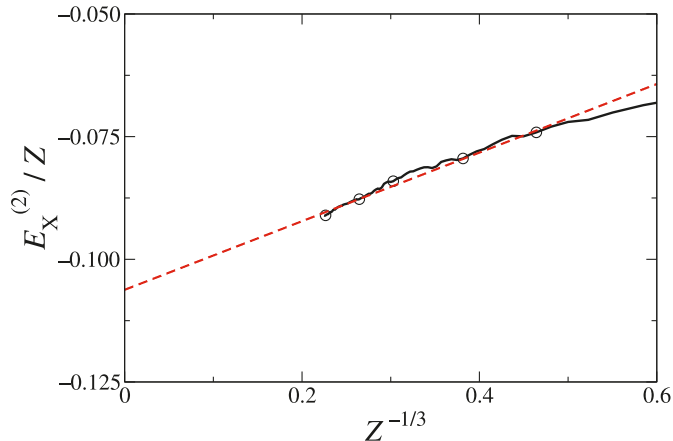
Fig. 6. The percentage error of the approximate asymptotic series given in eq. [13] is plotted as a function of Z. The error is remarkably low and demonstrates the power of these asymptotic series.
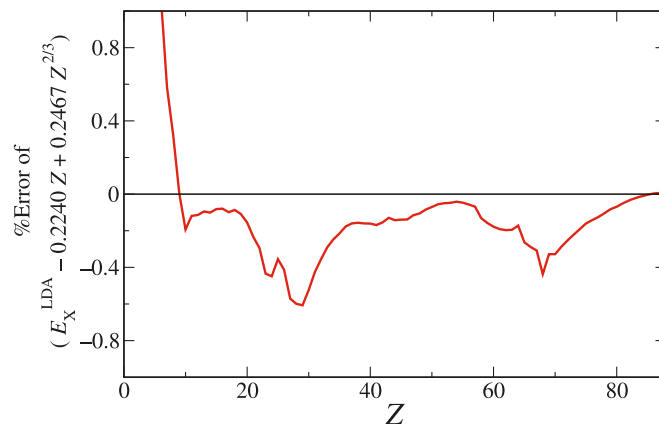

tions. Both popular GGAs recover (at least approximately) the accurate value. B88, designed specifically for molecular systems, is very close to the accurate value. PBE exchange is less so, but is also designed to bridge molecular and solid-state systems. The PBE value is between that of GEA and B88, but much closer to the latter than the former. Taking advantage of this insight, a new variation on PBE, called PBEsol,[30] restores the original gradient expansion, thereby worsening atomization energies (total energy differences), but improving many lattice constants of solids over PBE and LDA.

Deriving the β in B88

When designing a good GGA, one first chooses the functional form in terms of the dimensionless gradient s. This is usually based upon satisfying various constraints that the designer feels are important, e.g., reduce to LDA for $s = 0$, give correct asymptotic behavior for large r, prevent divergence for large s, and so forth. This is the most important step, and we do not discuss it in this paper, although work is ongoing in this direction.[16] After picking a functional form, there is usually still some freedom to choose any pa-

Table 1. $\Delta c = c_1 - c_1^{LDA}$ values for several different functionals.

	E_x	LDA	GEA	B88	PBE
Δc	–0.2240	—	–0.1062	–0.2216	–0.1946

Fig. 7. The percentage error for LDA, GEA and the modified GEA (MGEA) exchange functionals for $Z > 10$. The coefficient of $E_X^{(2)}$ is multiplied by 2.109 to make the MGEA AE1 asymptotically exact.
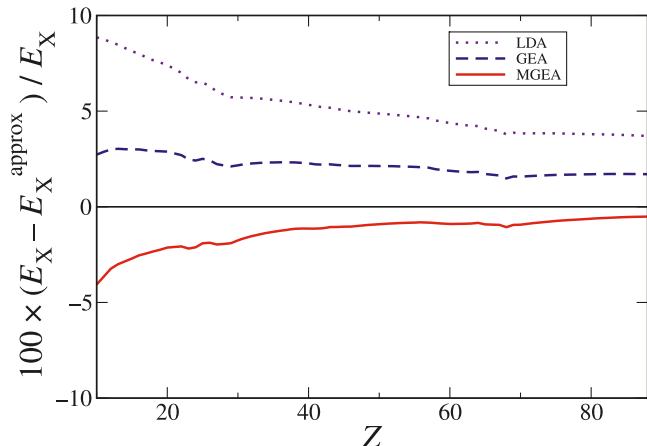
Fig. 8. We add to Fig. 7 the results for B88, PBE, and the excogitated B88 functional, all evaluated on the OEP exact exchange densities.
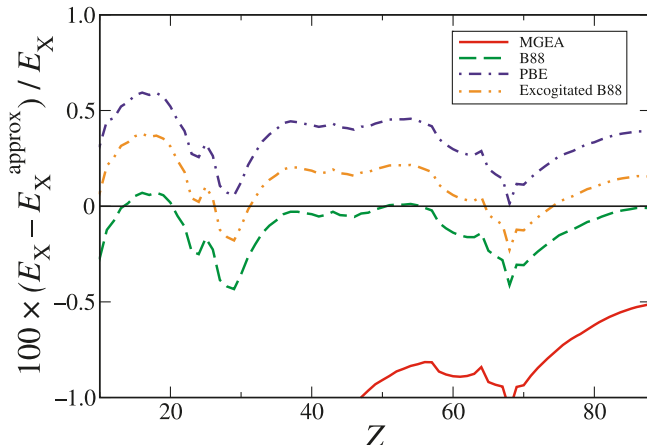
rameters (hopefully a small number) that may be left. These can be fixed by satisfying different exact constraints or by fitting to a set of experimental or computational data. The former is considered more favorable by some,[31] as it makes a functional more trustworthy for application to many different classes of systems, while the latter generally gives better properties for systems close to the fitting set. In the case of B88, we now show that the previously empirical parameter can be derived by requiring the exact condition that it be AE1. This explains why B88 was so successful when applied to different types of system.

The exchange energies found using GGAs such as B88 or PBE are generally dominated by their gradient expansion components for most chemically relevant densities (see Table 2 in ref. 12). Thus, to make B88 AE1, it is sufficient to impose this exact condition on just the $E_x^{(2)}[n]$ functional

form. Since both B88 and the GEA are built on top of LDA, we can simply look at the Δc values calculated above. If we set $\mu = 2.109\mu_{AK}$ in eq. [7], we multiply the c_1 coefficient of GEA by a factor of 2.109, making it AE1. In Fig. 7, we name this functional MGEA for modified GEA and plot its percentage errors. The values for LDA and GEA are also shown. It can be seen that modifying GEA to be AE1 has greatly reduced the error.

We now require that the B88 functional form, eq. [10], reduce to this MGEA for small values of x. Using eq. [9], this corresponds to using a value of $\beta = 0.0050$. Thus, we have derived an excogitated B88 that is free of any empirical parameters. The actual value used in B88 is $\beta^{B88} = 0.0053$ (for spin-polarized systems, this becomes 0.0042, which is the value given in ref. 7), so the values are very close. This is not surprising as fitting to Hartree–Fock exchange energies is an approximate way of demanding asymptotic exactness. Interestingly, the value quoted as the high-Z asymptote in ref. 7 and found using ref. 21 is essentially the same as our value, but was evidently rejected in favor of a better fit. In Fig. 8, we plot the percentage errors for B88, PBE, and the excogitated B88. As is typical for empirically fitted functionals, B88 performs very well for systems close to the data set used in the fitted procedure. Although the error for PBE is higher than both B88 and the excogitated B88, it is systematic in its overestimation. As noted, PBE was designed to perform reasonably well for a wide range of systems, so again, its behavior is not surprising. On this data set, the excogitated B88 was never going to do better than B88, although it remains to be seen how it performs for more complicated systems.

VI. Conclusion

We have carefully and systematically extracted the leading large-Z correction to the exchange energy of atoms. Our results differ slightly from those of ref. 12 but yield the same qualitative conclusion, i.e., that the gradient expansion yields an error of a factor of 2 or more for this coefficient. We have clarified some of the reasoning, and applied it more generally to any atom, molecule, or cluster. By looking in detail at the exchange energy asymptotic series for neutral atoms, we have demonstrated the power of using such series for functional development. Requiring that the small gradient expansion of B88 capture the two leading coefficients of the asymptotic expansion is a method by which the unknown coefficient β can be found. This gives a coefficient very close to the one actually used in B88, and thus is an *ex post facto* "derivation" of B88. Inserting our most accurate estimate for β into the B88 form yields an excogitated B88.

References

(1) Fiolhais, C.; Nogueira, F.; Marques, M., Eds.; *A Primer in Density Functional Theory;* Springer-Verlag: New York, 2003.

(2) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136* (3B), B864–B871. doi:10.1103/PhysRev.136.B864.

(3) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140* (4A), A1133–A1138. doi:10.1103/PhysRev.140.A1133.

(4) Antoniewicz, P. R.; Kleinman, L. *Phys. Rev. B* **1985**, *31* (10), 6779–6781. doi:10.1103/PhysRevB.31.6779.

(5) Ma, S.-K.; Brueckner, K. A. *Phys. Rev.* **1968**, *165* (1), 18–31. doi:10.1103/PhysRev.165.18.

(6) Rasolt, M.; Geldart, D. J. W. *Phys. Rev. B* **1986**, *34* (2), 1325–1328. doi:10.1103/PhysRevB.34.1325.

(7) Becke, A. D. *Phys. Rev. A* **1988**, *38* (6), 3098–3100. doi:10.1103/PhysRevA.38.3098. PMID:9900728.

(8) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37* (2), 785–789. doi:10.1103/PhysRevB.37.785.

(9) Becke, A. D. *J. Chem. Phys.* **1993**, *98* (7), 5648. doi:10.1063/1.464913.

(10) (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. doi:10.1103/PhysRevLett.77.3865. PMID:10062328.; (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78* (7), 1396. doi:10.1103/PhysRevLett.78.1396.

(11) (a) Schwinger, J. *Phys. Rev. A* **1980**, *22* (5), 1827–1832. doi:10.1103/PhysRevA.22.1827.; (b) Schwinger, J. *Phys. Rev. A* **1981**, *24* (5), 2353–2361. doi:10.1103/PhysRevA.24.2353.

(12) Perdew, J. P.; Constantin, L. A.; Sagvolden, E.; Burke, K. *Phys. Rev. Lett.* **2006**, *97* (22),o. 223002. doi:10.1103/PhysRevLett.97.223002. PMID:17155798.

(13) Englert, B.-G.; Schwinger, J. *Phys. Rev. A* **1985**, *32* (1), 26–35. doi:10.1103/PhysRevA.32.26. PMID:9896023.

(14) Lieb, E. H. *Rev. Mod. Phys.* **1981**, *53* (4), 603–641. doi:10.1103/RevModPhys.53.603.

(15) Lieb, E. H.; Simon, B. *Phys. Rev. Lett.* **1973**, *31* (11), 681–683. doi:10.1103/PhysRevLett.31.681.

(16) Elliott, P.; Lee, D.; Cangi, A.; Burke, K. *Phys. Rev. Lett.* **2008**, *100* (25),o. 256406. doi:10.1103/PhysRevLett.100.256406. PMID:18643686.

(17) Levy, M.; Perdew, J. P. *Phys. Rev. A* **1985**, *32* (4), 2010–2021. doi:10.1103/PhysRevA.32.2010. PMID:9896312.

(18) Froese-Fischer, C. *The Hartree–Fock method for atoms: A numerical approach;* Wiley: New York, 1977.

(19) Engel, E. *OPMKS, atomic DFT program;* University of Frankfurt: Germany.

(20) Perdew, J. P.; Schmidt, K. In *Density Functional Theory and Its Applications to Materials;* van Doren, V. E., van Alsenoy, K., and Geerlings, P., Eds.; American Institute of Physics: Melville, NY, 2001.

(21) Becke, A. D. *J. Chem. Phys.* **1986**, *84* (8), 4524. doi:10.1063/1.450025.

(22) Bowen, C.; Sugiyama, G.; Alder, B. J. *Phys. Rev. B* **1994**, *50* (20), 14838–14848. doi:10.1103/PhysRevB.50.14838.

(23) Moroni, S.; Ceperley, D. M.; Senatore, G. *Phys. Rev. Lett.* **1995**, *75* (4), 689–692. doi:10.1103/PhysRevLett.75.689. PMID:10060089.

(24) Lieb, E. H.; Oxford, S. *Int. J. Quantum Chem.* **1981**, *19* (3), 427–439. doi:10.1002/qua.560190306.

(25) Murphy, D. R. *Phys. Rev. A* **1981**, *24* (4), 1682–1688. doi:10.1103/PhysRevA.24.1682.

(26) Yan, Z. D.; Perdew, J. P.; Korhonen, T.; Ziesche, P. *Phys. Rev. A* **1997**, *55* (6), 4601–4604. doi:10.1103/PhysRevA.55.4601.

(27) Lee, D.; Constantin, L. A.; Perdew, J. P.; Burke, K. *J. Chem. Phys.* **2009**, *130* (3),o. 034107. doi:10.1063/1.3059783. PMID:19173510.

(28) Perdew, J. P. In *Electronic Structure of Solids '91;* Ziesche, P. and Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991, p. 11.

(29) Burke, K.; Perdew, J. P.; Wang, Y. In *Electronic Density Functional Theory: Recent Progress and New Directions;* Dobson, J. F., Vignale, G., and Das, M. P., Eds.; Plenum, NY, 1998; p. 81.

(30) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. *Phys. Rev. Lett.* **2008**, *100* (13),o. 136406. doi:10.1103/PhysRevLett.100.136406. PMID:18517979.

(31) Perdew, J. P.; Ruzsinszky, A.; Constantin, L. A.; Sun, J.; Csonka, G. I. *J. Chem. Theory Comput.* **2009**, *5* (4), 902–908. doi:10.1021/ct800531s.