We study the asymptotic expansion of the neutral-atom energy as the atomic number $Z \to \infty$, presenting a new method to extract the coefficients from oscillating numerical data. The correct expansion yields a condition on the Kohn–Sham kinetic energy that is important for the accuracy of approximate kinetic energy functionals for atoms, molecules, and solids. For example, this determines the small gradient limit of any generalized gradient approximation and conflicts somewhat with the standard gradient expansion. Tests are performed on atoms, molecules, and jellium clusters using densities constructed from Kohn–Sham orbitals. We also give a modern, highly accurate parametrization of the Thomas–Fermi density of neutral atoms.

I. INTRODUCTION

Ground-state Kohn–Sham (KS) density functional theory (DFT) is a widely used tool for electronic structure calculations of atoms, molecules, and solids,\(^1\) in which only the density functional for the exchange-correlation energy, $E_{\text{XC}}[n]$, must be approximated. But a direct, orbital-free DFT could be constructed if only the noninteracting kinetic energy $T_S$ were known sufficiently accurately as an explicit functional of the density.\(^2\) Using it would lead automatically to an asymptotic expansion of the Hartree energy $\hat{V}_{\text{ext}} + V_{\text{ee}}$, where $\hat{V}_{\text{ext}}$ is the kinetic energy operator, $V_{\text{ext}}$ is the external potential, and $V_{\text{ee}}$ is the electron-electron interaction, respectively. The electron density $n(r)$ yields \(N = \int d^3r n(r)\), where $N$ is the particle number.

To explain asymptotic exactness, we (re)introduce the $\zeta$-scaled potential\(^6\) (which is further discussed in Ref. 7),

\[ V_{\text{ext}}(r) = \zeta^{4/3} V_{\text{ext}}(\zeta^{4/3} r), \quad N \to \zeta N, \]

where $V_{\text{ext}}(r)$ is the external potential and the TF expectation value is $V_{\text{ext}}[n] = \zeta^{7/3} V_{\text{ext}}[n]$. In this $\zeta$-scaling scheme, nuclear positions $\mathbf{R}_a$ and charges $Z_a$ of molecules are scaled into $\zeta^{-1/3} \mathbf{R}_a$ and $\zeta Z_a$, respectively. In a uniform electric field $E \to \xi^{5/3} E$. For neutral atoms, scaling $\xi$ is the same as scaling $Z$, producing an asymptotic expansion for the total energy of neutral atoms,\(^4,8-11\)

\[ E = c_0 Z^{7/3} - c_1 Z^2 - c_2 Z^{5/3} + \cdots, \]

where $c_0 = 0.768 745$, $c_1 = -1/2$, $c_2 = 0.269 900$, and $Z$ is the atomic number. This large $Z$-expansion gives a remarkably good approximation to the Hartree–Fock energy of the neutral atoms, with less than a 10% error for $Z = 50$ and less than 0.5% error for $Z = 50$. By the virial theorem for neutral atoms $T = -E$ and $T = T_S$ to this order in the expansion (since the correlation energy is roughly $\sim Z$). Hence, the noninteracting kinetic energy has the following asymptotic expansion.

\[ T_S = c_0 Z^{7/3} + c_1 Z^2 + c_2 Z^{5/3} + \cdots. \]
We say that an approximation to the kinetic energy functional is asymptotically exact to the pth degree if it can reproduce the exact $c_0, c_1, \ldots, c_p$. The three displayed terms in Eq. (3) constitute the second-order asymptotic expansion for the total energy of neutral atoms, and we expect that this asymptotic expansion is a better starting point for constructing a more accurate approximation to the kinetic energy functional than the traditional gradient expansion approximation (GEA).

The leading term in Eq. (4) is given exactly by a local approximation to $T_S$ (TF theory), but the leading correction is due to higher-order quantum effects, and only approximated by the gradient expansion evaluated on the exact density. However, these coefficients are vital to finding accurate kinetic energies. Since we know that $c_0 Z^{7/3}$ becomes exact in a relative sense as $N = Z \rightarrow \infty$, we define $\Delta T_S = T_S - c_0 Z^{7/3}$ and investigate $\Delta T_S$ as a function of $Z$. How accurate is the asymptotic expansion for $\Delta T_S$? In Fig. 1, we evaluate $T_S$ for atoms (see Sec. III for details) and plot the percentage error in $\Delta T_S$, for all atoms and the asymptotic series with just two terms. The series is incredibly accurate, with only a 13% error for $N=2$ (He), and 14% for $N=1$. Thus, any approximation that reproduces the correct asymptotic series (up to and including the $c_2$ term) is likely to produce a highly accurate $T_S$.

To demonstrate the power and the significance of this approach, we apply it directly to the first term (where the answer is already known but perhaps not yet fully appreciated in the DFT community). Using any (all-electron) electronic structure code, one calculates the total energies of atoms for a sequence running down a column in the periodic table. By sticking with a specific column, one reduces the oscillatory contributions across rows, and the alkali-earth column yields the most accurate results. By then fitting the resulting curve of $T_S/Z^{7/3}$ as a function of $Z^{-1/3}$ to a parabola, one finds $c_0 = 0.7705$. Now assume one wishes to make a local density approximation (LDA) to $T_S$, but knows nothing about the uniform electron gas. Dimensional analysis (coordinate scaling) yields $^{12}$

$$ T^{0}[n] = A_S \tilde{I}, \quad \tilde{I} = \int d^3 r n^{8/3}(r), \quad (5) $$

but does not determine the constant, $A_S$. A similar fitting of $\tilde{I}$, based on the corresponding self-consistent densities, gives a leading term of 0.2677$Z^{7/3}$, yielding $A_S = 2.868$. Thus we have deduced the local approximation to the noninteracting kinetic energy.

A careful inspection of the above argument reveals that the uniform electron gas is never mentioned. As $N$ grows, the wavelength of the majority of the particles becomes short relative to the scale on which the potential is changing, loosely speaking, and semiclassical behavior dominates. The local approximation is a universal semiclassical result, which is exact for a uniform gas simply because that system has a constant potential. On the basis of that argument, we know that $A_S = (3/10)(3\pi^2)^{2/3} = 2.871$, demonstrating that (for this case) our result is accurate to about 0.1%. This argument tells us that the reliability of the local approximation is no indicator of how rapidly the density varies. That this argument is correct for neutral atoms was carefully proven by Lieb and Simon$^{13}$ in 1973 and later generalized by Lieb$^{6}$ for all matter.

The focus of the first part of this paper is on the remaining two known coefficients ($c_1$ and $c_3$) and how well the GEA performs for them. We evaluate those gradient terms by fitting asymptotic series and find that the traditional gradient expansion does well, but is not exact. From this information, we develop a modified gradient expansion approximation that reproduces the correct asymptotic coefficients $c_1$ and $c_3$, merely as an illustration of the power of asymptotic exactness. We test it on a variety of systems, finding the expected behavior.

In Sec. V, we present a parametrization of the TF density, which is more accurate than previous parametrizations. The TF density has a simple scaling with $Z$ and becomes relatively exact and slowly varying for a neutral atom as $Z \rightarrow \infty$, breaking down only near the nucleus and in the tail. We compare various quantities of our parametrization with exact values and earlier parametrizations and analyze the properties of the TF density.

### III. LARGE Z METHODOLOGY

We begin with a careful methodology for extracting the asymptotic behavior from highly accurate numerical calculations. Fully numerical DFT calculations were performed using the OPMKS code$^{14}$ to calculate the total energies of neutral atoms using ‘exact exchange’. This is simply minimizing the Hartree–Fock energy, subject to the constraint of a multiplicative potential.$^{15}$ The spin-density functional version of $T_S$ has been used for all systems.$^{16}$ We refer throughout to these...
as the KS results, and none of our analysis depends on which approximation we use. The coefficients $c_0$, $c_1$, and $c_2$ are the same over a wide range of approximations from exact exchange-correlation to local-density exchange.

To attain maximum accuracy for $c_1$ and $c_2$, we need to suppress the oscillations that come at the same order as the next term, $c_3Z^{4/3}$. Consider first the KS results ($T_S$). We investigate the differences between $T_S/Z^{7/3}$ and $c_0 + c_1Z^{-1/3} + c_2Z^{-2/3}$ in Fig. 2. We extract six data points [$Z=24$ (Cr), 25 (Mn), 30 (Zn), 31 (Ga), 61 (Pm), and 74 (W)], which have the smallest differences, i.e., nearest to where the curve crosses the horizontal axis. We then make a least-squares fit with a parabolic form in $Z^{-1/3}$, ignoring the oscillation term,

$$
\frac{T_S}{Z^{7/3}} = 0.768745 + c_1Z^{-1/3} + c_2Z^{-2/3}.
$$

(6)

Effectively, we solve two linear equations for $c_1$ and $c_2$. We explicitly include $c_0=0.768745$, since we do not have enough data points to extract $c_0$ accurately, especially in the region $Z^{-1/3} < 0.2$. It is important to control the behavior of the fitting line at $Z \to \infty$. This fitting yields an accurate estimate of $c_1 = -0.5000$ and $c_2 = 0.2702$, with error less than 1%, demonstrating the accuracy of our method for $c_1$ and $c_2$.

We repeat the same procedure to extract $c_1$ and $c_2$ coefficients of TF and second- and fourth-order GEAAs, which are given by

$$
T^{\text{GEA}2} = T^{\text{TF}} + T^{(2)},
$$

(7)

and

$$
T^{\text{GEA}4} = T^{\text{TF}} + T^{(2)} + T^{(4)}.
$$

(8)

These gradient corrections to the local approximation are given by

$$
T^{(2)} = \frac{5}{27} \int d^3 r \tau^{\text{TF}}(r)s^2(r),
$$

(9)

and

$$
T^{(4)} = \frac{8}{81} \int d^3 r \tau^{\text{TF}}(r) \left[ q^2(r) - \frac{9}{8} q(r)s^2(r) + \frac{s^4(r)}{3} \right],
$$

(10)

where $\tau^{\text{TF}}(r)$, $s(r)$, and $q(r)$ are defined as

$$
\tau^{\text{TF}}(r) = \frac{\nabla n(r)}{2k_f(r)n(r)},
$$

(12)

$$
q(r) = \frac{\nabla^2 n(r)}{4k_f^2(r)n(r)},
$$

(13)

and $k_f(r) = (3\pi^2 n(r))^{1/3}$.

We have also applied this procedure to both $T^{(2)}$ and $T^{(4)}$. Since the asymptotic expansions of these energies begin at $Z^2$, we extract only a $c_1$ and a $c_2$ for each using the following equations:

$$
\frac{T^{\text{GEA}2} - T^{\text{TF}}}{Z^{7/3}} = \Delta c_1 Z^{-1/3} + \Delta c_2 Z^{-2/3},
$$

(14)

and

$$
\frac{T^{\text{GEA}4} - T^{\text{GEA}2}}{Z^{7/3}} = \Delta c_1 Z^{-1/3} + \Delta c_2 Z^{-2/3}.
$$

These results are also included in Table I and are of course consistent with our results from Eq. (6).

### IV. RESULTS AND INTERPRETATION

To understand the meaning of the above results, begin with the values of $c_1$. We have combined the results of the $T^{(2)}$ and $T^{(4)}$ fits with that of the $T^{\text{TF}}$ fit to produce the asymptotic coefficients of $T^{\text{GEA}2}$ and $T^{\text{GEA}4}$. We check that these combinations produce the same coefficients in Table I which are found from the direct fitting of $T^{\text{GEA}2}$ and $T^{\text{GEA}4}$ using Eq. (6). The exact value of $c_1$ is $-1/2$. We see that the local approximation (TF) gives a good estimate, $-0.66$. Then the second-order gradient expansion yields $-0.54$, reducing the error by a factor of 5. Finally, the fourth-order

---

**Table II. KS kinetic energy ($T$) in hartrees and various approximations for alkali-earth atoms.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>$Z$</th>
<th>$T_S$</th>
<th>$T_{\text{TF}}$</th>
<th>% error</th>
<th>$T^{\text{GEA}2}$</th>
<th>% error</th>
<th>$T^{\text{MGEA}2}$</th>
<th>% error</th>
<th>$T^{\text{GEA}4}$</th>
<th>% error</th>
<th>$T^{\text{MGEA}4}$</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>4</td>
<td>14.5724</td>
<td>13.1290</td>
<td>-10</td>
<td>14.6471</td>
<td>0.5</td>
<td>15.0880</td>
<td>3.5</td>
<td>14.9854</td>
<td>2.8</td>
<td>14.5453</td>
<td>-0.2</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>199.612</td>
<td>184.002</td>
<td>-8</td>
<td>198.735</td>
<td>-0.4</td>
<td>203.014</td>
<td>1.7</td>
<td>201.452</td>
<td>0.9</td>
<td>199.924</td>
<td>0.2</td>
</tr>
<tr>
<td>Ca</td>
<td>20</td>
<td>676.752</td>
<td>630.604</td>
<td>-7</td>
<td>672.740</td>
<td>-0.6</td>
<td>685.136</td>
<td>1.2</td>
<td>680.286</td>
<td>0.5</td>
<td>677.433</td>
<td>0.1</td>
</tr>
<tr>
<td>Sr</td>
<td>38</td>
<td>3131.53</td>
<td>2951.89</td>
<td>-6</td>
<td>3110.44</td>
<td>-0.7</td>
<td>3156.50</td>
<td>0.8</td>
<td>3136.76</td>
<td>0.2</td>
<td>3134.48</td>
<td>0.09</td>
</tr>
<tr>
<td>Ba</td>
<td>56</td>
<td>7883.53</td>
<td>7478.27</td>
<td>-5</td>
<td>7829.36</td>
<td>-0.7</td>
<td>7931.34</td>
<td>0.6</td>
<td>7886.19</td>
<td>0.03</td>
<td>7888.14</td>
<td>0.06</td>
</tr>
<tr>
<td>Ra</td>
<td>88</td>
<td>23094.3</td>
<td>22065.8</td>
<td>-4</td>
<td>22945.9</td>
<td>-0.6</td>
<td>23201.5</td>
<td>0.5</td>
<td>23083.9</td>
<td>-0.05</td>
<td>23110.5</td>
<td>0.07</td>
</tr>
</tbody>
</table>
gradient expansion yields $-0.52$, a further improvement, yielding only a 4% error in its approximation to the Scott correction.\(^\text{19}\)

For $c_2$, the gradient expansion is less useful. The exact result is 0.27, while the TF approximation overestimates this as 0.39. The GEA2 result is only slightly reduced (0.34), and the fourth-order correction has the wrong sign.

To understand how important these results can be, we consider how exchange and correlation functionals are constructed. Often, such constructions begin from the GEA, which is then generalized to include (in an approximate way) all powers of a given gradient. For slowly varying densities, it is considered desirable to recover the GEA result. However, we have seen here how this conflicts with the asymptotic expansion, and in Ref. 5, it was shown how the asymptotic expansion is more significant to energies of real materials and how successful GGAs for atoms and molecules well-approximate the large-$Z$ asymptotic result not the slowly varying gas.

**A. Atoms**

To illustrate this point, we construct here a trivial modified gradient expansion, MGEA2, designed to have the correct asymptotic coefficients, in so far as is possible. Thus

$$T^{\text{MGEA2}} = T^\text{TF} + 1.290T^{(2)}.$$  \tag{15}

The enhancement coefficient has been chosen to make $c_1^{\text{MGEA2}} = -1/2$. In Table II, we list the results of several different approximations for the alkali-earth atoms. Because the GEA2 error passes through 0 around $Z=8$, its errors are artificially low.

We can repeat this exercise for the fourth order, matching both $c_1$ and $c_2$ to exact values. Now we find:

$$T^{\text{MGEA4}}[n] = T^\text{TF}[n] + 1.789T^{(2)}[n] - 3.841T^{(4)}[n],$$  \tag{16}

i.e., strongly modified gradient coefficients. This is somewhat arbitrary, as there are several terms in $T^{(4)}$, and there is no real reason to keep their ratios the same as in GEA [Eq. (10)]. However, the results of Table II and Fig. 3 speak for themselves. The resulting functional is better than either GEA for all the alkali earths. Of course, $T_3$ is positive for any density, as are the terms $T^\text{TF}$, $T^{(2)}$, and $T^{(4)}$ of the GEA. Equation (16) however can be improperly negative for rapidly varying densities, and so is not suitable for general use.

**TABLE III.** Noninteracting kinetic energy (in hartrees) for molecules, and errors in approximations. All values are evaluated on the converged KS orbitals and densities obtained with B88-PW91 functionals, and the MGEA4 kinetic energies are evaluated using the TF and the GEA data from Ref. 20.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$T_3$</th>
<th>$T^\text{TF}$</th>
<th>$T^{\text{GEA2}}$</th>
<th>$T^{\text{GEA4}}$</th>
<th>$T^{\text{MGEA4}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.500</td>
<td>$-0.044$</td>
<td>0.011</td>
<td>0.032</td>
<td>$-0.026$</td>
</tr>
<tr>
<td>B</td>
<td>24.548</td>
<td>$-2.506$</td>
<td>$-0.058$</td>
<td>0.476</td>
<td>$-0.177$</td>
</tr>
<tr>
<td>C</td>
<td>37.714</td>
<td>$-3.731$</td>
<td>$-0.154$</td>
<td>0.600</td>
<td>$-0.228$</td>
</tr>
<tr>
<td>N</td>
<td>54.428</td>
<td>$-4.993$</td>
<td>$-0.097$</td>
<td>0.904</td>
<td>$-0.078$</td>
</tr>
<tr>
<td>O</td>
<td>74.867</td>
<td>$-6.990$</td>
<td>$-0.546$</td>
<td>0.765</td>
<td>$-0.497$</td>
</tr>
<tr>
<td>F</td>
<td>99.485</td>
<td>$-9.093$</td>
<td>$-0.933$</td>
<td>0.659</td>
<td>$-0.609$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>1.151</td>
<td>$-0.142$</td>
<td>$-0.014$</td>
<td>0.033</td>
<td>$-0.094$</td>
</tr>
<tr>
<td>HF</td>
<td>100.169</td>
<td>$-9.016$</td>
<td>$-0.920$</td>
<td>0.639</td>
<td>$-0.520$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>76.171</td>
<td>$-7.074$</td>
<td>$-0.692$</td>
<td>0.565</td>
<td>$-0.484$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>40.317</td>
<td>$-3.773$</td>
<td>$-0.140$</td>
<td>0.619</td>
<td>$-0.189$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>56.326</td>
<td>$-5.292$</td>
<td>$-0.400$</td>
<td>0.587</td>
<td>$-0.331$</td>
</tr>
<tr>
<td>BF$_3$</td>
<td>323.678</td>
<td>$-29.052$</td>
<td>$-2.641$</td>
<td>2.454</td>
<td>$-1.370$</td>
</tr>
<tr>
<td>CN</td>
<td>92.573</td>
<td>$-8.940$</td>
<td>$-0.687$</td>
<td>0.978</td>
<td>$-0.570$</td>
</tr>
<tr>
<td>CO</td>
<td>112.877</td>
<td>$-10.694$</td>
<td>$-0.911$</td>
<td>1.036</td>
<td>$-0.670$</td>
</tr>
<tr>
<td>F$_2$</td>
<td>199.023</td>
<td>$-18.367$</td>
<td>$-2.201$</td>
<td>0.925</td>
<td>$-1.451$</td>
</tr>
<tr>
<td>HCN</td>
<td>92.982</td>
<td>$-8.925$</td>
<td>$-0.658$</td>
<td>1.008</td>
<td>$-0.534$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>109.013</td>
<td>$-10.487$</td>
<td>$-0.916$</td>
<td>0.999</td>
<td>$-0.719$</td>
</tr>
<tr>
<td>NO</td>
<td>129.563</td>
<td>$-12.342$</td>
<td>$-1.240$</td>
<td>0.962</td>
<td>0.279</td>
</tr>
<tr>
<td>O$_2$</td>
<td>149.834</td>
<td>$-14.186$</td>
<td>$-1.527$</td>
<td>0.965</td>
<td>$-1.110$</td>
</tr>
<tr>
<td>MAEb</td>
<td>9.364</td>
<td>0.872</td>
<td>0.812</td>
<td>0.600</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Ref. 20.

$^b$Mean absolute error.
B. Molecules

The improvement in total kinetic energies is not just confined to atoms. Also, for noninteracting kinetic energies of molecules, using the data in Ref. 20, Eq. (16) gives a better average of the absolute errors in hartrees (0.6) than $T_{\text{TF}}$ (9.4), $T_{\text{GEA}^2}$ (0.9), and $T_{\text{GGA}}$ (0.8), shown in Table III. Of greater importance are energy differences. For atomization kinetic energies, also using the data in Ref. 20, $T_{\text{TF}}$ gives the best averaged absolute error (0.25), which is worsened by gradient corrections. Since the GEA does not have the right quantum corrections from the edges, turning points and Coulomb cores, GEA does not improve on the atomization process. However, the TF kinetic energy functional is always the dominant term. So, TF gives very good results on the atomization kinetic energies. But the error (0.29) of Eq. (16) is smaller than that of $T_{\text{GEA}^2}$ (0.36) and $T_{\text{GGA}}$ (0.44). In either case, Eq. (16) works better for atoms and molecules than the fourth-order gradient expansion. Thus, requiring asymptotic exactness is a useful and powerful constraint in functional design.

C. Jellium surfaces

We test this MGEA4 functional for jellium surface kinetic energies. As shown in Table IV, the $T_{\text{TF}}$ term in $T_{\text{GGA}}$ improves the jellium surface kinetic energy in comparison to the results of $T_{\text{GEA}^2}$, but Eq. (16) worsens the jellium surface kinetic energies due to the strongly modified coefficient of $T_{\text{TF}}$. This is a confirmation of our general approach. By building in the correct asymptotic behavior for atoms, including the Scott correction coming from the 1s region, we worsen energetics for systems without this feature.

D. Jellium spheres

We also investigate the kinetic energies of neutral jellium spheres (with KS densities using LDA exchange-correlation and with $r_s=3.9$) from Ref. 21. The analysis of the results is based upon the liquid drop model of Refs. 22 and 23. We write

$$T_3(r_s,N) = \frac{4}{3} \pi R^3 \rho_{\text{unif}}(r_s) + 4 \pi R^2 \sigma_s + 2 \pi R \gamma_s^\text{eff}(r_s,N),$$

(17)

where $R$ is the radius of the sphere of uniform positive background. Since we know the bulk (uniform) kinetic energy density $\rho_{\text{unif}}$ and the surface kinetic energy $\sigma_s$ for a given functional, we can extract $\gamma_s^\text{eff}(r_s,N)$ from this equation, and

$$\lim_{N \to \infty} \gamma_s^\text{eff}(r_s,N) = \gamma_s(r_s)$$

(18)

is the curvature energy of jellium. We calculate $\gamma_s^\text{eff}(r_s,N)$ using the TF, GEA, MGEA, and a Laplacian-level meta-GGA (LmGGA) of Ref. 21, which is explained further in the following subsection. From Table V, we observe that: (i) gradient corrections in GEA worsen $\gamma_s^\text{eff}$, (ii) the LmGGA of Ref. 21 is even worse than $T_{\text{GGA}^4}$, (iii) Eq. (15) (which has the right $c_0$ and $c_1$) is not so good, but better than $T_{\text{GGA}^4}$, and (iv) Eq. (16) (which has the right $c_0$, $c_1$, and $c_2$) gives good results.

E. Existing approximations

We suggest that the large-Z asymptotic expansion is a necessary condition that an accurate kinetic energy functional should satisfy, but is not sufficient. We show this by testing two kinds of semilocal approximations (GGA and meta-GGA) to the kinetic energy functionals.

Recently, Tran and Wesolowski24 constructed a GGA-type kinetic energy functional using the conjointness conjecture. They found the enhancement factor by minimizing mean absolute errors of kinetic energies for closed-shell atoms. We evaluate the kinetic energies of atoms using this functional ($T_{\text{GGA}}$) and extract the asymptotic coefficients

| TABLE IV. Jellium surface kinetic energies (erg/cm$^2$) and % error, which is $(\sigma_s^{\text{app}} - \sigma_s^\text{ex})/\sigma_s^\text{ex}$, of each approximation. |
|---|---|---|---|---|---|---|
| $r_s$ | Exact | $T_{\text{TF}}$ | $T_{\text{GEA}^2}$ | $T_{\text{GGA}}$ | $T_{\text{MGEA}^2}$ | $T_{\text{MGEA}^4}$ | $T_{\text{LmGGA}}$ |
| 2 | $-5492.7$ | 11 | 2.5 | 1.1 | $-0.9$ | 0.73 | 1.3 |
| 4 | $-139.9$ | 54 | 22 | 11 | 12 | 36 | 15 |
| 6 | $-3.4$ | 660 | 330 | 180 | 238 | 675 | 280 |

-- See Eq. (15).

-- See Eq. (16).

| TABLE V. 10$^4$ $(\gamma_s^\text{eff}(r_s,N) - \gamma_s^\text{TF}(r_s,N))$ in atomic units vs $N=Z$ for neutral jellium spheres with $r_s=3.93$ with various functionals. As $N \to Z \to \infty$, $\gamma_s^\text{eff}$ tends to the curvature kinetic energy of jellium, $\gamma_s$. |
|---|---|---|---|---|---|
| $N$ | Exact | $T_{\text{GEA}^2}$ | $T_{\text{GGA}}$ | $T_{\text{MGEA}^2}$ | $T_{\text{MGEA}^4}$ | $T_{\text{LmGGA}}$ |
| 2 | $-1.8$ | 1.1 | 2.4 | 1.5 | $-2.8$ | 1.9 |
| 8 | $-1.9$ | 1.0 | 2.1 | 1.3 | $-2.3$ | 5.1 |
| 16 | $-0.5$ | 1.2 | 2.0 | 1.6 | $-0.7$ | 6.4 |
| 58 | $-0.8$ | 1.3 | 2.2 | 1.7 | $-1.1$ | 3.2 |
| 92 | $-1.7$ | 1.2 | 2.0 | 1.5 | $-1.0$ | 1.9 |
| 254 | $-0.5$ | 1.4 | 2.3 | 1.8 | $-0.9$ | ... |

-- See Eq. (15).

-- See Eq. (16).
The good

We calculate the asymptotic coefficients shown in Table I for fourth-order gradient expansion in the slowly varying limit. These values are better than those of the GEA's. In fact, from studies of the asymptotic series,25 it is known that the shell-structure occurs in the next order, $Z^{4/3}$, and that the noble gases are furthest from the asymptotic curves. However, Table VI shows our functionals work almost as well for the noble gas series.

\[ n(r) = \frac{Z^2}{4\pi a^2} \left( \frac{\Phi}{x} \right)^{3/2}, \]

where $a=(1/2)(3\pi/4)^{2/3}$ and $x=Z^{1/3}r/a$, and the dimensionless TF differential equation is

\[ \frac{d^2\Phi(x)}{dx^2} = \sqrt{\frac{\Phi(x)}{x}}, \quad \Phi(x) > 0, \]

which satisfies the following initial conditions:

\[ \Phi(0) = 1, \quad \Phi'(0) = -B, \quad B = 1.5880710226. \]

We construct a model for $\Phi$, which recovers the first eight terms of the small-$x$ expansion and the leading term of the asymptotic expansion at large-$x$ ($\Phi(x) \rightarrow 144/x^3$, as $x \rightarrow \infty$). Following Tal and Levy,28 we use $y=\sqrt{x}$ as the variable, because of the singularity of the TF equation. Our parametrization is

\[ \Phi^{\text{mod}}(y) = \left( 1 + \sum_{p=2}^{9} \alpha_p y^p \right) \left/ \left( 1 + y^9 \sum_{p=1}^{5} \beta_p y^p + \frac{\alpha_0 y^{15}}{144} \right) \right., \]

where $\alpha_i$ and $\beta_i$ are coefficients given in the Table VII. The values of $\alpha_i$ are fixed by the small-$y$-expansion, while those of $\beta_i$ are found by minimization of the weighted sum of squared residuals $\chi^2$ for $0 < y < 10$. The $\chi^2$ was minimized using the Levenberg–Marquardt method.29 This method is for fitting when the model depends nonlinearly on the set of unknown parameters. 1000 points were used, equally spaced between $y=0$ and $y=10$. We plot the accurate $\Phi(y)$ and our model in Fig. 4, and the differences between them in Fig. 5. These graphs illustrate the accuracy of our parametrization.

![Fig. 4. Accurate numerical $\Phi(y)$ and parametrized $\Phi(y)$ cannot be distinguished.](image)

TABLE VI. KS kinetic energy ($T$) in hartrees and various approximations for noble atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$Z$</th>
<th>$T_S$</th>
<th>$T_{\text{TF}}$</th>
<th>$%$ error</th>
<th>$T_{\text{GDA}}$</th>
<th>$%$ error</th>
<th>$T_{\text{GDA}^2}$</th>
<th>$%$ error</th>
<th>$T_{\text{GDA}^4}$</th>
<th>$%$ error</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2</td>
<td>2.86168</td>
<td>2.56051</td>
<td>-11</td>
<td>2.87847</td>
<td>0.6</td>
<td>2.97083</td>
<td>3.8</td>
<td>2.96236</td>
<td>3.5</td>
</tr>
<tr>
<td>Ne</td>
<td>10</td>
<td>128.545</td>
<td>117.761</td>
<td>-8</td>
<td>127.829</td>
<td>-0.6</td>
<td>130.753</td>
<td>1.7</td>
<td>129.737</td>
<td>0.9</td>
</tr>
<tr>
<td>Ar</td>
<td>18</td>
<td>526.812</td>
<td>489.955</td>
<td>-7</td>
<td>524.224</td>
<td>-0.5</td>
<td>534.178</td>
<td>1.4</td>
<td>530.341</td>
<td>0.7</td>
</tr>
<tr>
<td>Kr</td>
<td>36</td>
<td>2752.04</td>
<td>2591.20</td>
<td>-6</td>
<td>2733.07</td>
<td>-0.7</td>
<td>2774.27</td>
<td>0.8</td>
<td>2756.72</td>
<td>0.2</td>
</tr>
<tr>
<td>Xe</td>
<td>54</td>
<td>7232.12</td>
<td>6857.94</td>
<td>-5</td>
<td>7183.78</td>
<td>-0.7</td>
<td>7278.42</td>
<td>0.6</td>
<td>7236.65</td>
<td>0.06</td>
</tr>
<tr>
<td>Rn</td>
<td>86</td>
<td>21866.7</td>
<td>20885.7</td>
<td>-4</td>
<td>21725.4</td>
<td>-0.6</td>
<td>21969.3</td>
<td>0.5</td>
<td>21857.2</td>
<td>-0.04</td>
</tr>
</tbody>
</table>

V. MODERN PARAMETRIZATION OF THOMAS–FERMI DENSITY

Our asymptotic expansion study gives new reasons for studying large $Z$ atoms. Our approximate functionals were tested on highly accurate densities, but ultimately, self-consistency is an important and more demanding test. Any approximate functional yields an approximate density via the Euler equation. In this section, we present a new, modern parametrization of the neutral atom TF density, which is more accurate than earlier versions.26,27

The TF density of a neutral atom can be written as

\[ \Phi(x) = \sum_{i=1}^{9} \left( 1 + \sum_{p=2}^{9} \alpha_p y^p \right) \left/ \left( 1 + y^9 \sum_{p=1}^{5} \beta_p y^p + \frac{\alpha_0 y^{15}}{144} \right) \right., \]

where $\alpha_i$ and $\beta_i$ are coefficients given in the Table VII. The values of $\alpha_i$ are fixed by the small-$y$-expansion, while those of $\beta_i$ are found by minimization of the weighted sum of squared residuals $\chi^2$ for $0 < y < 10$. The $\chi^2$ was minimized using the Levenberg–Marquardt method.29 This method is for fitting when the model depends nonlinearly on the set of unknown parameters. 1000 points were used, equally spaced between $y=0$ and $y=10$. We plot the accurate $\Phi(y)$ and our model in Fig. 4, and the differences between them in Fig. 5. These graphs illustrate the accuracy of our parametrization.
In Table VIII we calculate several moments using our model and existing models that were proposed by Gross and Dreizler\textsuperscript{26} and Latter\textsuperscript{27}. The Latter parametrization is

\[ \Phi^{GD}(x) = 1/(1 + 1.4712x - 0.4973x^{3/2} + 0.3875x^{2} + 0.002 102x^{3}) \]  

and the Gross–Dreizler model (which correctly removes the \(\sqrt{x}\) term) is:

\[ \Phi^{GD}(x) = 1/(1 + 1.4712x - 0.4973x^{3/2} + 0.3875x^{2} + 0.002 102x^{3}) \]  

(24)

Lastly, we introduce an extremely simple model that we have found useful for pedagogical purposes (even when \(N\) differs from \(Z\)). We write

\[ n_{\text{ped}}(r) = \frac{N}{2\pi^{3/2}R^{3/2}}e^{-r/R}, \quad R = \frac{\alpha N^{2/3}}{Z - \beta N}, \]  

(25)

where \(\alpha = (9/5)(\sqrt{3/4!})^{1/3}\) and \(\beta = 1/2 - 1/\pi\) have been found from integration of the TF kinetic and Hartree energies, respectively, and \(R\) minimizes the TF total energy. For \(N=Z\), this yields:

\[ \Phi_{\text{ped}}(x) = \gamma e^{-2\alpha(1-\beta)x^{3/2}}, \quad \gamma = \frac{5\sqrt{2}}{6\sqrt{3}}\left(\frac{1}{2} + \frac{1}{\pi}\right). \]  

(26)

This crude approximation does not satisfy the correct initial conditions of Eq. (21),

\[ \Phi_{\text{ped}}(0) = \gamma = 0.880 361(\neq 1), \]  

\[ \Phi_{\text{ped}}'(0) = -\frac{125(2 + \pi^{2})}{648(4\pi^{3})^{1/3}} = -0.48(\neq -1.59). \]  

(27)

To compare the quality of the various parametrizations, we calculate the \(p\)th moment of the \(j\)th power of \(\Phi(x)/x\),

\[ M_{j}^{(p)} = \int dx x^{p}(\Phi(x)/x)^{j}. \]  

(28)

Many quantities of interest can be expressed in terms of these moments.

1. Particle number: To ensure \(\int d^{3}r n(r) = N\), we require

\[ M_{3/2}^{(2)} = 1. \]  

(29)

2. TF kinetic energy: The TF kinetic energy is \(c_{0}Z^{7/3}\), which implies

\[ M_{3/2}^{(2)} = \frac{5}{4}B. \]  

(30)

3. The Hartree energy is \(U = (1/2)\int d^{3}r d' r' (n(r) n(r')/r - r') = (1/7a)M_{3/2}^{(2)}Z^{7/3}\), which implies

\[ M_{3/2}^{(1)} = B. \]  

(31)

4. The external energy is defined as \(V_{ext} = -\int d^{3}r Zn(r)/r = -(1/3a)M_{3/2}^{(2)}Z^{7/3}\) for the exact TF density, which also implies Eq. (31).

5. The LDA exchange energy is defined as \(E_{X}^{\text{LDA}} = A_{x}\int dr n^{4/3}(r)\), where \(A_{x} = -(3/4)(3/\pi)^{1/3}\), so for TF, \(E_{X}^{\text{LDA}} = A_{x}(4\pi a^{3})^{-1/3}M_{3/2}^{(2)}Z^{7/3}\), which implies

\[ M_{3/2}^{(2)} = 0.615 434 679, \]  

(32)

extracted from our accurate numerical solution. LDA exchange suffices\textsuperscript{4,5} for asymptotic exactness to the order displayed in Eqs. (3) and (4); for a numerical study, see Ref. 30.

Table VIII shows that our modern parametrization is far more accurate than existing models by all measures, and that our simple pedagogical model is roughly correct for many features. Finally, we make some comparisons with densities of real atoms to illustrate those features of real atoms that are captured by TF. The radial density \(s(r)\) [Eq. (12)] and \(q(r)\) [Eq. (13)] are given by

\[ 4\pi^{2}n(r) = Z^{1/3}/f(x)/a, \]  

(33)

where \(f(x) = \sqrt{x\Phi^{3/2}(x)}\),

\[ s(r) = \frac{a_{1}}{Z^{1/3}/f(x)}, \quad a_{1} = (9/2\pi)^{1/3}/2, \]  

(34)

and

<table>
<thead>
<tr>
<th>Moment</th>
<th>Our model</th>
<th>% error</th>
<th>Gross and Dreizler\textsuperscript{a}</th>
<th>% error</th>
<th>Latter\textsuperscript{b}</th>
<th>% error</th>
<th>(\Phi_{\text{mod}}(x)/x)</th>
<th>% error</th>
<th>Exact</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_{3/2}^{(2)})</td>
<td>0.999 857 885</td>
<td>-0.01</td>
<td>1.008</td>
<td>0.8</td>
<td>0.999</td>
<td>-0.04</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>(M_{3/2}^{(2)})</td>
<td>1.134 264 62</td>
<td>-0.006</td>
<td>1.129</td>
<td>-0.4</td>
<td>1.137</td>
<td>0.2</td>
<td>1.11</td>
<td>-2</td>
<td>5B/7</td>
</tr>
<tr>
<td>(M_{3/2}^{(2)})</td>
<td>0.615 438 208</td>
<td>0.001</td>
<td>0.612</td>
<td>-0.4</td>
<td>0.616</td>
<td>0.02</td>
<td>0.72</td>
<td>16</td>
<td>0.615 434 679\textsuperscript{a}</td>
</tr>
<tr>
<td>(M_{3/2}^{(1)})</td>
<td>1.587 998 57</td>
<td>-0.005</td>
<td>1.584</td>
<td>-0.2</td>
<td>1.589</td>
<td>0.07</td>
<td>1.62</td>
<td>2</td>
<td>B</td>
</tr>
</tbody>
</table>
FIG. 6. Plot of the scaled radial densities of Ba and Ra using Eq. (33) and SCF densities. TF scaled densities of Ba and Ra are on top of each other.

\[ q(r) = \frac{a_2^2}{3Z^{2/3}} \left\{ g(x) + 2x^2\Phi(x)\Phi'(x) \right\}, \]  \hspace{1cm} (35)

where \( g(x) \) is defined as \( \Phi(x) - x\Phi'(x) \). The gradient relative to the screening length is

\[ \tau(r) = \frac{\|\nabla n(r)\|}{2k_s(r)n(r)}, \quad \text{where} \quad k_s(r) = \sqrt{4k_F(r)/\pi}, \]  \hspace{1cm} (36)

and here

\[ \tau(r) = \frac{a_2|g(x)|}{(x^3\Phi^5(x))^{1/4}}, \quad a_2 = \frac{3^{5/6}n^{1/3}}{2^{8/3}\sqrt{\pi}} = 0.6124. \]  \hspace{1cm} (37)

We also show large- and small-x limit behaviors of various quantities using \( \Phi(x) \rightarrow 144/x^3 \) as \( x \rightarrow \infty \) and \( \Phi(x) \rightarrow 1 - Bx + \cdots \) as \( x \rightarrow 0 \).

\[ \frac{Z^2}{4\pi a^3} \left( \frac{1}{x^2} - \frac{1}{x^3} \right) n(r) \sim 432Z^2, \]  \hspace{1cm} (38)

\[ \frac{Z^{2/3}}{a} \left( \frac{\sqrt{x} - 4\pi^2n(r)}{x} - \frac{44Z^{2/3}}{ax^{5/2}} \right), \]  \hspace{1cm} (39)

\[ \frac{a_1}{Z^{1/3}} \sqrt{x} \sim s(r) \sim \frac{a_1x}{3Z^{1/3}}, \]  \hspace{1cm} (40)

\[ \frac{a_1}{Z^{2/3}} \sqrt{x} \sim q(r) \sim \frac{5a_1^2x^2}{54Z^{2/3}}, \]  \hspace{1cm} (41)

\[ \frac{a_2}{x^{3/4}} \sim t(r) \sim \frac{2a_3}{\sqrt{3}}. \]  \hspace{1cm} (42)

We plot the \( Z \)-scaled accurate self-consistent densities and TF radial densities of Ba \((Z=56)\) and Ra \((Z=88)\) in Fig. 6. Although the shell structure is missing, and the decay at a large distance is wrong, the overall shape of the TF density is relatively correct.

In Figs. 7–9, we plot the scaled \( s(r) \), \( q(r) \), and \( t(r) \) using the self-consistent and TF densities of Ba and Ra. In particular, \( t(r) \) measures how fast the density changes on the scale of the TF screening length, and its magnitude does not vary with \( Z \) in TF theory. From these figures, we see that \( s(r) \), \( q(r) \), and \( t(r) \) of the TF density diverge near the nucleus, since the TF density does not satisfy Kato’s cusp condition.

When \( N=Z \rightarrow \infty \) for a realistic density, \( s(r) \) is small except in the density tail \((s \sim Z^{-1/3} \text{ over most of the density})\), and \( q(r) \) is small except in the tail and 1s core regions \((q \sim Z^{-2/3} \text{ over most of the density})\). This is why gradient expansions for the kinetic and exchange energies, applied to realistic densities, work as well as they do in this limit. The kinetic and exchange energies have only one characteristic length scale, the local Fermi wavelength, but the correlation energy also has a different one, the local screening length. Since \( t(r) \) is not and does not become small in this limit, gradient expansions do not work well at all for the correlation energies of atoms. The standard of “smallness” for \( s \) and \( q \), and the more severe standard of smallness for \( t \), are explained in Refs. 5 and 31.

Finally we evaluate \( T^{(0)} + T^{(2)} \) on the TF density. We find the correct \( c_0 \) in the \( Z \rightarrow \infty \) expansion from \( T^{(0)} \) but \( c_1 \) vanishes, due to the absence of a proper nuclear cusp, and \( c_2 \) diverges because \( T^{(2)} \) diverges at its lower limit of integration.
VI. SUMMARY

We have shown the importance of the large-$N$ limit for density functional construction of the kinetic energy (with the functional evaluated on a KS density), and also provided a modern, highly accurate parameterization of the neutral-atom TF density. Our results should prove useful in the never-ending search for improved density functionals.

For atoms and molecules, the large-$N$ limit seems more important than the slowly varying limit. On the ladder of density-functional approximations, there are three rungs of semilocal approximations, there are three rungs of nonlocal ones, followed by higher rungs of fully nonlocal ones. The LDA uses only the local density, the GGA uses also the density gradient, and the meta-GGA uses the orbital kinetic energy density or the Laplacian of the density. For the exchange-correlation energy, the GGA rung cannot simultaneously describe the slowly varying limit and the density functional construction of the kinetic energy and the TF density. Our results should prove useful in the development in Quantum Chemistry, edited by J. L. Paz and A. J. Hernandez (Research Signpost, Kerala, in press).


E. Engel, op.mks, atomic DFT program, University of Frankfurt, Germany.


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KS kinetic energy and TF density