

# Relations between coordinate and potential scaling in the high-density limit

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(Received 29 June 2004; accepted 25 January 2005; published online 7 April 2005)

Exact relations are derived between scaling to the high-density limit of density functional theory and taking  $Z$  to infinity for nondegenerate atoms. Görling–Levy perturbation results are deduced for hydrogenic densities. The kinetic contribution to the correlation energy is also studied, and estimates given for its value for neutral atoms. Popular approximate functionals are tested against these benchmarks. © 2005 American Institute of Physics. [DOI: 10.1063/1.1872832]

## I. INTRODUCTION

The validity of density functional theory (DFT) and the range of problems to which it may be applied are well established.<sup>1</sup> However, the usefulness of predicted quantities is limited by the accuracy and reliability of density functional approximations to the exchange–correlation energy,<sup>2</sup> hence the constant need for more accurate functionals. Although many exact constraints have already been determined and incorporated into the construction of functionals,<sup>3</sup> there is great interest in additional conditions that functionals should satisfy. Testing in extreme limits allows us to explore the limitations of functional approximations.

Scaling of the electronic density is often used to test functional behavior. Under uniform coordinate scaling, a density is either squeezed into a smaller region or spread out over a larger region, but retains its shape. Exact behavior under scaling is known for all components of the energy except the correlation energy, for which an inequality has been derived.<sup>4</sup> Most approximate functionals are developed to satisfy these scaling relations. Scaling is simply related to the adiabatic connection<sup>5,6</sup> which is the basis for constructing hybrid functionals and understanding their success.<sup>7–9</sup>

There are quantum chemistry benchmarks for correlation energies of various isoelectronic series,<sup>10,11</sup> i.e., sets of ions with the same numbers of electrons. Analogous benchmarks do not exist for DFT despite their potential usefulness. In this paper we consider the behavior of the correlation energy in the high-density limit when the nuclear charge  $Z$  becomes infinitely large. In many ways, the effect is similar to that of scaling in DFT.

One important difference between coordinate scaling and scaling by increasing the nuclear charge of ions is the change in the shape of the density with  $Z$ . These changes must be accounted for, and produce small but significant correction terms to the usual scaling expansion coefficients when relating them to the coefficients of scaling in  $Z$ . Although the densities become hydrogenic as  $Z \rightarrow \infty$ , corrections appear at higher orders in  $1/Z$ . It would be useful to have benchmarks on hydrogenic densities because the ability of functionals to reproduce these benchmarks is a means of

testing their accuracy in the high-density limit. There is a beautiful simplification of the expression of the high- $Z$  correlation coefficients in terms of the Görling–Levy (GL) coefficients when the sum of kinetic and total correlation energies is considered. This makes the method more easily applicable for testing and is a simple and fairly accurate method for extracting  $T_c[n]$ , the kinetic contribution to the correlation energy.  $T_c[n]$  is defined as the difference between the kinetic energy of the physical system  $T[n]$  and that of the Kohn–Sham system  $T_s[n]$ .

Herein we determine, to second order in  $1/Z$ , the expansion coefficients of the correlation energy for nondegenerate ions, of the density for  $N=2$ -,  $3$ -, and  $10$ -electron ions, and of the correlation potential for  $N=2$ -electron ions. The correlation energy coefficients were determined by a least squares fit to correlation energy data reported in the literature.<sup>10,11</sup> The density coefficients were obtained from exact exchange calculations using Engel’s atomic DFT code.<sup>12</sup> Finally, the correlation potential coefficients were extracted from Umrigar and Gonze’s Quantum Monte Carlo (QMC) calculations for  $2$ -electron ions.<sup>13,14</sup>

For nondegenerate systems, the correlation energy scales to a constant.<sup>15</sup> Not all approximate correlation functionals scale correctly to the high-density limit. The local density approximation<sup>16</sup> (LDA) violates this condition. The long-range nature of the Coulomb interaction in an infinite system (the uniform electron gas) leads to a logarithmic divergence.<sup>17,18</sup> The parameterization of the Perdew–Wang 1991 (PW91) functional<sup>19</sup> fails to capture the correct behavior, but the Perdew–Burke–Ernzerhof (PBE) correlation functional was designed to correct this.<sup>18</sup> The PBE functional yields good results for the correlation energy of these large- $Z$  atoms.

## II. SCALING IN DENSITY FUNCTIONAL THEORY

A method widely used in density functional theory to discover exact properties of functionals is the study of their behavior under uniform scaling of the electron density  $n(\mathbf{r})$ . A scale factor  $\gamma$  is introduced that changes the length scale of the density while maintaining normalization. A scaled density is defined as

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$$n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma\mathbf{r}), \quad (1)$$

and the behavior of functionals is studied when  $\gamma$  is varied between 0 and  $\infty$ . We will limit our discussion to the usual case in which the Kohn–Sham (KS) wave function associated with  $n(\mathbf{r})$  is a single Slater determinant, i.e., the KS system is nondegenerate. In such systems, the exact exchange functional satisfies  $E_x[n_\gamma] = \gamma E_x[n]$ , as does any reputable approximation to it. Only inequalities and limiting cases have been proven so far for the scaling behavior of the correlation energy:

$$E_c[n_\gamma] > \gamma E_c[n], \quad \gamma > 1. \quad (2)$$

The energy at different coupling constants  $\lambda$  (keeping  $n$  fixed) can also be given in terms of the scaled density:<sup>20–23</sup>

$$E_{xc}^\lambda[n] = \lambda^2 E_{xc}[n_{1/\lambda}]. \quad (3)$$

The adiabatic connection provides a continuous link between the physical and Kohn–Sham systems by varying the strength of the interaction while keeping the density fixed. The high-density limit ( $\gamma \rightarrow \infty$ ) corresponds to a weak  $\lambda$ .<sup>5,6</sup> Hybrid functionals are constructed by analyzing the dependence on  $\lambda$  and replacing a portion of the approximate density functional for exchange with exact exchange.<sup>8,9</sup>

Scaling to the high-density limit is particularly simple in DFT, and a perturbation theory has been developed to take advantage of it. For the nondegenerate case, Levy<sup>15</sup> shows

$$E_c[n_\gamma] = E_c^{[2]}[n] + \frac{1}{\gamma} E_c^{[3]}[n] + \frac{1}{\gamma^2} E_c^{[4]}[n] + \dots, \quad (4)$$

where each  $E_c^{[p]}[n]$  is a *scale-independent* functional, i.e.,  $E_c^{[p]}[n_\gamma] = E_c^{[p]}[n]$ . Görling and Levy<sup>24</sup> developed a perturbation theory for these functionals.

It would be natural to equate  $\gamma$  above with  $Z$  in large- $Z$  atoms, as both quantities perform the same under dimensional analysis and many functions tend to the same value as either  $Z$  or  $\gamma \rightarrow \infty$ . But a crucial difference is that in coordinate scaling, the density does not change shape, while as  $Z \rightarrow \infty$ , it does. We show below that this difference is irrelevant at zeroth order, but requires careful treatment for all orders beyond that.

### III. LARGE- $Z$ ATOMS

We consider the behavior of ions of fixed electron number  $N$  as  $Z \rightarrow \infty$ . Results for these systems are well known<sup>10,11,25</sup> in wave function theory for many values of  $Z$ . Many quantities can be expanded as a function of  $1/Z$  once their large- $Z$  behavior is understood. We consider only those atoms that do not exhibit degeneracies in the  $Z = \infty$  limit. For all others, Linderberg and Shull show that in the high- $Z$  limit, the energies of these atoms become degenerate and the correlation energy does not approach a constant.<sup>26</sup>

Begin with the correlation energy. For an atom whose outermost electron is in a nondegenerate orbital, the quantum-chemical correlation energy, defined as the difference between an exact nonrelativistic quantum mechanical ground-state energy and a Hartree–Fock (HF) energy, tends to a finite limit as  $Z \rightarrow \infty$ . Thus we may write

TABLE I. Correlation energy coefficients of  $1/Z$  expansion for select electron number  $N$  in milliHartrees. Obtained by least squares fit to the initial slope of  $E_c$  as a function of  $1/Z$  from data of Refs. 10 and 11.

$N$	$E_c^{(2)}$	$E_c^{(3)}$	$E_c^{(4)}$
2	-46.67	9.98	-1.4
3	-53.62	25.1	-0.6
7	-236.9	353	-93
8	-306.0	446	-210
9	-369.1	521	-540
10	-428.2	601	-1400
11	-460.2	793	-900

$$E_c^{\text{QC}}(Z) = E_c^{(2)} + \frac{E_c^{(3)}}{Z} + \frac{E_c^{(4)}}{Z^2} + \dots, \quad Z \rightarrow \infty. \quad (5)$$

We use superscript parentheses to denote powers of  $1/Z$ , but have shifted these powers by 2 to coincide with the usual DFT notation in Eq. (4).

We must now address the difference between the quantum chemical and DFT definitions of correlation energy.<sup>15,27</sup> Following Levy,<sup>15</sup> we can consider two distinct origins of this difference. For a given density, in the absence of degeneracies, the Kohn–Sham wave function is the Slater determinant that minimizes the kinetic energy operator for a given density. The HF wave function, however, minimizes both kinetic and electron–electron repulsion energies, but its orbitals do not arise from a single multiplicative potential, in general. This difference vanishes for  $N=2$  (we consider only spin saturated systems) but, by construction, the HF energy is more negative than the DFT exchange energy for a given density of other  $N$ . This difference has been found to be very small numerically.<sup>28</sup> A second difference occurs because, in the quantum-mechanical definition, the HF energy is evaluated on the self-consistent HF density, which differs from the exact density. This is a difference for all  $N$ , including  $N=2$ .

The bulk of the data useful for our study are those of Davidson and co-workers in a series of extremely careful studies of the total energies of atoms and ions of various  $Z$ . These include accurate HF calculations, yielding  $E_c^{\text{QC}}$ . Only in the special case of  $N=2$  do we also have accurate data for the DFT correlation energy, and also for the densities and exchange–correlation potentials as a function of  $Z$ .

Table I lists the coefficients of the high- $Z$  quantum-chemical correlation energy expansion for various atoms. These were determined by a quadratic least squares fit of the initial slope of correlation energy as a function of inverse nuclear charge data.<sup>10,11</sup> For series with  $N > 7$ , points furthest from the origin were selectively removed and a least squares fit performed with each omission. This procedure was repeated until the values of the coefficients had converged, resulting in the inclusion of only points corresponding to  $Z \geq 17$  in the final fit. The maximum absolute difference between our quadratic fit, with the coefficients given in Table I, and any single point is 0.04 mH.

The leading term  $E_c^{(2)}[n]$  is an extrapolation to  $1/Z=0$  and is the most accurate term given in the table. The accuracy of our predicted coefficients decreases with order, with a large uncertainty for the second-order correction term,

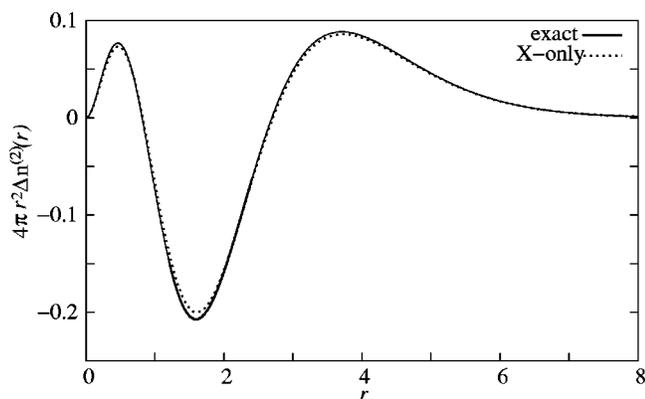


FIG. 1. Second-order correction to the density,  $\Delta n^{(2)}(\mathbf{r})$ , for 2-electron ions. The solid line is the exact curve extracted from Umrigar's data (Refs. 13 and 14). The dashed line is the self-consistent exact exchange-only result (Ref. 12).

$E_c^{(4)}[n]$ . The numbers agree with data previously published,<sup>25,29-31</sup> except for the sodium series, whose value was incorrectly reported in Ref. 31.

We also calculated the expansion coefficients for the DFT correlation energy of the two-electron series.<sup>14</sup> We find identical results for the first two contributions, but  $E_c^{(4)}[n] = 1.4$  instead of 1.7. Thus the difference between the HF and exact densities is measurable here. We have no data to estimate this difference for the other series.

The density can also be expanded in powers of  $1/Z$ :

$$n(Z; \mathbf{r}) = Z^3 \{ n_H(Z\mathbf{r}) + \Delta n^{(1)}(Z\mathbf{r})/Z + \Delta n^{(2)}(Z\mathbf{r})/Z^2 + \dots \}, \quad (6)$$

the leading term being the density of a hydrogenic atom with  $N$  electrons. The quantities  $n_H(\mathbf{r})$ ,  $\Delta n^{(1)}(\mathbf{r})$ , and  $\Delta n^{(2)}(\mathbf{r})$  are all independent of  $Z$  and finite.

We calculated these using Engel's numerical atomic code<sup>25</sup> that calculates energies and other quantities for atoms using density functional methods. For our calculation of the densities, we use exact exchange only. This yields the hydrogenic density and the first correction term  $\Delta n^{(1)}(\mathbf{r})$  exactly, and gives a very accurate second-order correction term in comparison to Umrigar's data for  $N=2$  (see Fig. 1). Figures 2-4 show the expansion coefficients for the helium, lithium,

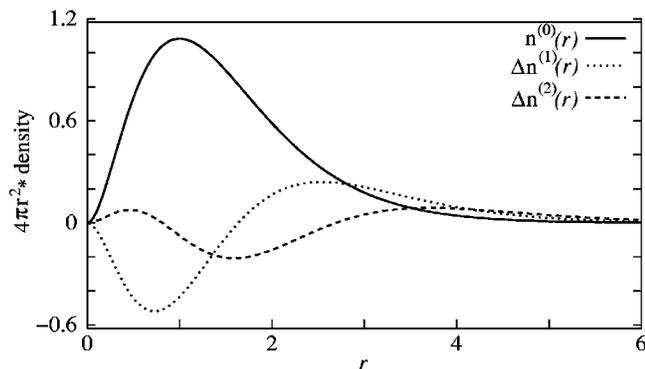


FIG. 2. Coefficients of density expansion in  $1/Z$  for the helium isoelectronic series: the leading term (the hydrogenic density for two electrons) (solid line), the coefficient of the leading correction (short dashes), and the coefficient of the second-order correction (long dashes).

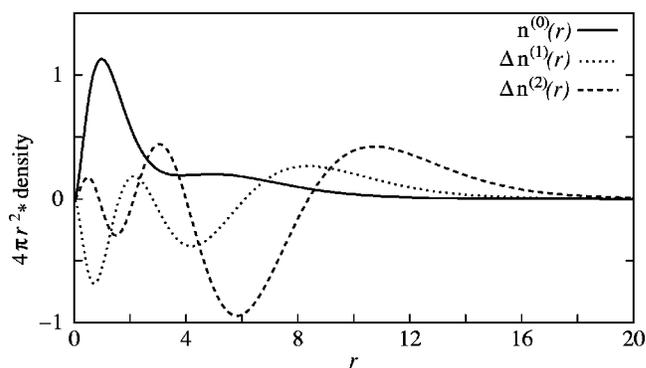


FIG. 3. Same as Fig. 2, but for the lithium isoelectronic series.

and neon isoelectronic densities. The corrections to the hydrogenic densities get comparatively larger as the number of electrons increases.

Lastly, we extract the large- $Z$  limit expansion of the correlation potential:

$$v_c[n](Z; \mathbf{r}) = v_c^{(2)}(Z\mathbf{r}) + \frac{v_c^{(3)}(Z\mathbf{r})}{Z} + \frac{v_c^{(4)}(Z\mathbf{r})}{Z^2} + \dots, \quad Z \rightarrow \infty. \quad (7)$$

Figure 5 shows the large- $Z$  limit expansion coefficients of the correlation potential for the helium isoelectronic series.

#### IV. RELATION BETWEEN DIFFERENT LIMITS

In this section, we carefully derive the relationships between the large- $Z$  expansion and the high-density limit of density functional theory. These relationships are derived for the DFT correlation energy, kinetic-correlation energy, and potentials, and we extract numbers for the two-electron ion series from Umrigar's data. Applications of these relations to quantum chemical data for  $N > 2$  must also account for the difference in definitions of correlation energy, especially beyond first order. In addition to the expansion of the energy and density, we also need the expansion of the correlation potential,  $v_c[n(Z; \mathbf{r})]$ . From the definition of the functional derivative, one can show

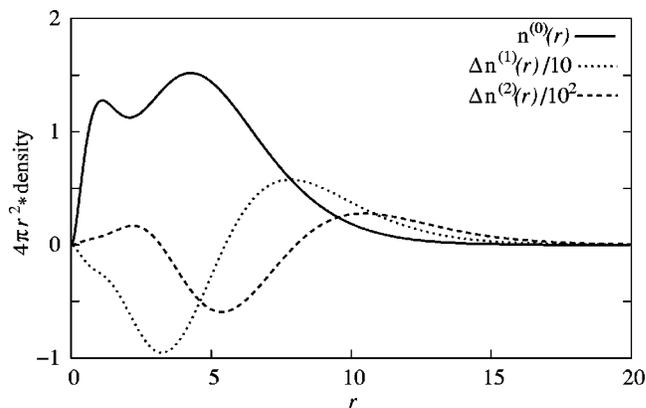


FIG. 4. Same as Fig. 2, but for the neon isoelectronic series.

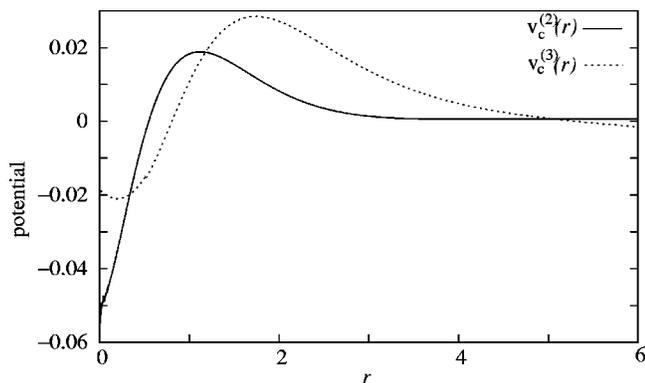


FIG. 5. Expansion coefficients for Umrigar's correlation potential for the helium isoelectronic series: the leading term  $v_c^{(2)}(\mathbf{r})$  (solid line), the coefficient of the first-order correction term  $v_c^{(3)}(\mathbf{r})$  (short dashes), the coefficient of the second-order correction term  $v_c^{(4)}(\mathbf{r})$  (long dashes).

$$v_c[n_\gamma]\left(\frac{\mathbf{r}}{\gamma}\right) = \frac{\delta E_c[n_\gamma]}{\delta n(\mathbf{r})}. \quad (8)$$

Thus, in the high-density limit, from Eq. (4),

$$\begin{aligned} v_c[n_\gamma]\left(\frac{\mathbf{r}}{\gamma}\right) &= \frac{\delta E_c^{[2]}[n]}{\delta n(\mathbf{r})} + \frac{1}{\gamma} \frac{\delta E_c^{[3]}[n]}{\delta n(\mathbf{r})} + \dots \\ &= v_c^{[2]}[n](\mathbf{r}) + \frac{1}{\gamma} v_c^{[3]}[n](\mathbf{r}) + \dots. \end{aligned} \quad (9)$$

Applying this expansion to the large- $Z$  limit and substituting Eq. (6), we obtain

$$\begin{aligned} v_c\left(Z; \frac{\mathbf{r}}{Z}\right) &= v_c\left[\left(n_H(\mathbf{r}) + \frac{1}{Z}\Delta n^{(1)}(\mathbf{r}) + \dots\right)_{\gamma=Z}\right]\left(\frac{\mathbf{r}}{Z}\right) \\ &= v_c^{[2]}[n](\mathbf{r}) + \frac{1}{Z} v_c^{[3]}[n](\mathbf{r}) + \dots. \end{aligned} \quad (10)$$

Since  $\Delta n^{(1)}(\mathbf{r})/Z$  is a small perturbation on  $n_H(\mathbf{r})$ , and

$$v_c^{[2]}[n + \Delta n](\mathbf{r}) = v_c^{[2]}[n](\mathbf{r}) + \int d^3r' f_c^{[2]}[n](\mathbf{r}, \mathbf{r}') \Delta n(\mathbf{r}'), \quad (11)$$

where  $f_c^{[2]}[n](\mathbf{r}, \mathbf{r}')$  is the second functional derivative of the leading term in the GL expansion,  $E_c^{[2]}[n]$ , then to first order in  $1/Z$ ,

$$\begin{aligned} v_c[n(Z; \mathbf{r})]\left(\frac{\mathbf{r}}{Z}\right) &= v_c^{[2]}[n_H](\mathbf{r}) + \frac{1}{Z} \left\{ v_c^{[3]}[n_H](\mathbf{r}) \right. \\ &\quad \left. + \int d^3r' \Delta n^{(1)}(\mathbf{r}) f_c^{[2]}[n_H](\mathbf{r}, \mathbf{r}') \right\} + \dots. \end{aligned} \quad (12)$$

We deduce

$$v_c^{(2)}[n_H](\mathbf{r}) = v_c^{[2]}[n_H](\mathbf{r}) \quad (13)$$

and

$$v_c^{(3)}[n_H](\mathbf{r}) = v_c^{[3]}[n_H](\mathbf{r}) + \int d^3r' \Delta n^{(1)}(\mathbf{r}) f_c^{[2]}[n_H](\mathbf{r}, \mathbf{r}'). \quad (14)$$

Thus the leading term in the correlation potential as  $Z \rightarrow \infty$  is exactly the high-density limit of the correlation potential of the hydrogenic density, but this is not true for the first correction.

We are ready to deduce formulas for the coefficients of the  $1/Z$  expansion in Eq. (5). As previously shown,<sup>30</sup>

$$E_c^{(2)} = \lim_{Z \rightarrow \infty} E_c[Z^3 n_H(Z\mathbf{r}) + \dots] = E_c^{[2]}[n_H]. \quad (15)$$

This shows that, in the high-density limit, the correlation energy approaches the GL second-order correlation energy coefficient, evaluated on the hydrogenic density for a given number of electrons. Similarly,

$$E_c^{(3)} = \lim_{Z \rightarrow \infty} Z[E_c(Z) - E_c^{(2)}]. \quad (16)$$

Expanding  $n(Z; \mathbf{r})$  around  $n_{H,Z}(\mathbf{r})$ , the hydrogenic density, substituting, and taking the limit, we obtain

$$E_c^{(3)} = E_c^{[3]}[n_H] + \int d^3r \Delta n^{(1)}(\mathbf{r}) v_c^{[2]}[n_H](\mathbf{r}). \quad (17)$$

Thus the next terms in the two expansions *differ*, due to the change in shape of the density. Continuing to the next order, we find several corrections

$$\begin{aligned} E_c^{(4)} &= E_c^{[4]}[n_H] + \int d^3r \Delta n^{(1)}(\mathbf{r}) v_c^{[3]}[n_H](\mathbf{r}) \\ &\quad + \int d^3r \Delta n^{(2)}(\mathbf{r}) v_c^{[2]}[n_H](\mathbf{r}) \\ &\quad + \frac{1}{2} \int d^3r \int d^3r' \Delta n^{(1)}(\mathbf{r}) \Delta n^{(1)}(\mathbf{r}') f_c^{[2]}[n_H](\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (18)$$

To second order the correlation energy is a sum of GL correlation energy coefficients evaluated on the hydrogenic density and integrals over their derivatives and corrections to the hydrogenic density. In density functional terms, changes in  $E_c$  due to changes in nuclear charge are accompanied by changes in the electronic density.

Next we discuss how further information can be extracted from highly accurate quantum calculations on atoms for large  $Z$ , if another key quantity,  $T_c$ , is available. This quantity is not usually calculated by standard codes. In fact,  $T_c$  can be extremely demanding to calculate, as it involves a small difference between two large numbers. In particular, one needs the noninteracting kinetic energy of the Kohn–Sham orbitals corresponding to the exact density. The kinetic energy of a Hartree–Fock calculation will yield a good approximation, but not good enough for reliable values for  $T_c$ . Fortunately, Umrigar has calculated  $T_c$  for the two-electron series for many values of  $Z$ .

We can write expressions for the high-density limit expansion of  $T_c$  similar to those of  $E_c$  in Sec. III and IV. Thus  $T_c[n]$  may be expanded in the high-density limit in terms of

TABLE II. Coefficients of expansion of  $T_c$  and  $E_c$  for 2-electron ions, calculated using Eq. (15), (17), and (21)–(24).

Quantity	Value (mH)
$T_c^{(2)}$	46.7
$T_c^{(3)}$	-21.5
$T_c^{(4)}$	2.7
$E_c^{(3)}$	10.0
$\int d^3r \Delta n^{(1)} v_c^{[2]}(\mathbf{r})$	-1.8
$E_c^{[2]}$	-46.7
$E_c^{[3]}$	11.5±0.5

scale-independent functionals  $T_c^{[p]}[n]$ , as in Eq. (4); or  $T_c(Z)$  can be expanded around  $Z \rightarrow \infty$  in terms of  $T_c^{(p)}$ , as in Eq. (5). If we define its potential by

$$v_{T_c}[n](\mathbf{r}) = \frac{\delta T_c[n]}{\delta n(\mathbf{r})} \quad (19)$$

and expand it around  $Z \rightarrow \infty$ , we find analogs of Eqs. (15), (17), and (18) relating the two expansions for  $T_c$ .

However, the kinetic correlation and correlation energies are related by scaling:<sup>32</sup>

$$\gamma \frac{dE_c[n_\gamma]}{d\gamma} = E_c[n_\gamma] + T_c[n_\gamma]. \quad (20)$$

As determined by Görling and Levy,<sup>24</sup> expanding Eq. (20) around  $\gamma \rightarrow \infty$  we find that the high-density limit of the kinetic contribution is simply

$$T_c^{[p]}[n] = -(p-1)E_c^{[p]}[n], \quad p = 2, 3, 4, \dots, \quad (21)$$

and that

$$v_{T_c}^{[p]}[n](\mathbf{r}) = -(p-1)v_c^{[p]}[n](\mathbf{r}). \quad (22)$$

Particularly useful is the fact that  $v_{T_c}^{[2]}[n] = -v_c^{[2]}[n]$ , so that the potential corrections to  $E_c^{(3)} + T_c^{(3)}$  cancel, yielding

$$E_c^{(3)} + T_c^{(3)} = E_c^{[3]} + T_c^{[3]} = -E_c^{[3]}[n_H], \quad (23)$$

that is, expansion of  $E_c + T_c$  in powers of  $1/Z$  yields  $E_c^{[3]}[n_H]$  directly. Similarly all integrals with potentials of order 2 in the next order term cancel, yielding

$$E_c^{(4)} + T_c^{(4)} = -2E_c^{[4]} - \int d^3r \Delta n^{(1)}(\mathbf{r}) v_c^{[3]}[n_H](\mathbf{r}), \quad (24)$$

a less useful result.

The high-density limit expansion was first tested on the helium isoelectronic series for which Umrigar and co-workers<sup>13,14,33</sup> have calculated exact values for the density and potential as well as  $E_c$  and  $T_c$ . The components necessary to evaluate  $E_c(Z) + T_c(Z)$  were extracted. Table II lists the coefficients of  $T_c$  and  $E_c$  expansion in  $1/Z$  and the corresponding Görling–Levy coefficients for two electrons. Note that in this limit the  $T_c^{(2)}$  and  $E_c^{(2)} = E_c^{[2]}$  terms cancel as expected.

One can also write a virial expression for  $E_c[n] + T_c[n]$ :

TABLE III. Exact (Refs. 10 and 11), our expansion-constructed extrapolation [determined by substituting coefficients from Table I and  $Z=N$  in Eq. (5)], and the Morrison and Zhao (Ref. 34) correlation energies of neutral atoms in milliHartrees.

$N$	Exact	Extrapolation	Extrapolation percentage error	MZ	MZ percentage error
2	-42.04	-42.05	<1	-42.02	<1
3	-45.33	-45.32	<1	-45.17	<1
7	-188.31	-188.4	<1	-180.5	-4
8	-257.94	-253.6	-2	-244.3	-5
9	-324.53	-317.8	-2	-307.1	-5
10	-390.47	-382.3	-2	-378.9	-3
11	-395.64	-395.5	<1	-381.1	-4

$$-\int d^3r n(\mathbf{r}) \mathbf{r} \cdot \nabla v_c(\mathbf{r}) = E_c[n] + T_c[n]. \quad (25)$$

This virial may also be expanded in  $1/Z$  to give a leading term

$$-\int d^3r n_H(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^{[2]}[n_H](\mathbf{r}) = 0 \quad (26)$$

and a first-order correction

$$-\int d^3r \{n_H(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^{(3)}(\mathbf{r}) + \Delta n^{(1)}(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^{(2)}(\mathbf{r})\} = E_c^{(3)} + T_c^{(3)}. \quad (27)$$

This first-order virial correction may be written in terms of GL coefficients:

$$\int d^3r \{n_H(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^{[3]}(\mathbf{r}) + \Delta n^{(1)}(\mathbf{r}) \mathbf{r} \cdot \nabla v_c^{[2]}(\mathbf{r})\} = E_c^{[3]}[n_H]. \quad (28)$$

Differentiating Eq. (25), the kinetic correlation may also be expressed in terms of a virial of total correlation potentials and derivatives:

$$v_{T_c}[n](\mathbf{r}) = -v_c[n](\mathbf{r}) - \mathbf{r} \cdot \nabla v_c[n](\mathbf{r}) - \int d^3r' n(\mathbf{r}') \mathbf{r}' \cdot \nabla f_c[n](\mathbf{r}, \mathbf{r}'). \quad (29)$$

## V. NEUTRAL ATOMS

In this section, we use insight gained from the exact large- $Z$  limit to deduce approximate results for  $Z=N$ , thereby demonstrating that such studies have practical as well as methodological implications.

Correlation energies for a few atoms are listed in Table III. The correlation energy is consistently underestimated by the Morrison and Zhao<sup>34</sup> (MZ) estimate, which are determined from configuration interaction calculated reference densities using Slater-type orbital basis sets.<sup>11,35,36</sup> The MZ estimate is good for small electron number, but its error consistently increases with electron number. This indicates the difficulty in calculating correlation energies rather than correlation energy differences. Our expansion-constructed cor-

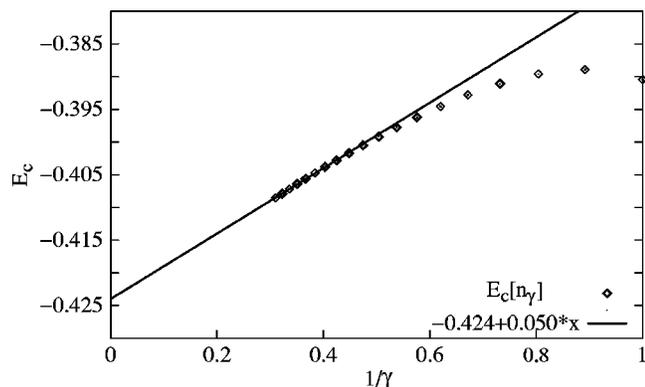


FIG. 6. Correlation energy of the ten-electron series with  $\gamma$  estimated from  $Z$ . The line represents the initial slope and is assumed to be the slope at  $\gamma = 1$  when estimating  $E_c[n_\gamma] + T_c[n]$ .

relation energy is an extrapolation from the high-density limit to the physical ( $Z=N$ ) limit. We take the correlation energy coefficients determined in Table I and substitute  $Z=N$  into Eq. (5). The errors in the extrapolated correlation energies for neutral atoms are smaller than those due to basis sets in the MZ estimate, indicating that the series converges rapidly.

As mentioned in the preceding section, accurate calculation of  $T_c$  is very demanding, and only limited results are available in the literature. In particular, Morrison and Zhao used a clever algorithm to construct the exact Kohn–Sham potential and orbitals for the densities discussed above.<sup>37–39</sup> This produced a list of  $T_c$  for neutral atoms up to argon.

If we ignore changes in shape of the density, we can approximate  $E_c[n_\gamma]$  by  $E_c(Z)$ , equating changes with  $Z$  with changes with  $\gamma$ . That is, the change in shape of the density caused only a 15% error in the correlation energy first-order correction term  $E_c^{[3]}$ . This method was used by Frydel, Terrilla, and Burke,<sup>32</sup> but a correction using the potential was used there, making it extremely accurate. The correction is not accessible here, requiring as it does the correlation potential.

We must still devise a method for choosing the “best” relation between  $Z$  and  $\gamma$ . We know that under exact scaling

$$\gamma = \frac{E_X[n_\gamma]}{E_X[n]} = \sqrt{\frac{T_s(Z^*)}{T_s(Z)}}, \quad (30)$$

where  $T_s(Z^*)$  is the KS kinetic energy at  $Z \neq N$ . We can approximate the latter relationship with ease for atomic ions. In

TABLE IV.  $E_c[n_\gamma] + T_c[n]$  in millihenry, where  $N$  is the number of electrons. Extrapolation obtained using Eq. (20).

$N$	Exact <sup>a</sup>	Extrapolation	MZ <sup>b</sup>	PBE	LYP
2	-5.5	-5.7	-5	-4.3	-9.9
3		-9.0	-7	-4.6	-14.8
7		-50	-30	-22	-64
8		-55	-50	-34	-81
9		-53	-70	-40	-90
10	-65.0	-50	-80	-45	-98
11		-92	-70	-44	-102

<sup>a</sup>References 13 and 14.

<sup>b</sup>Reference 34.

TABLE V.  $T_c[n]$  in milliHartrees, where  $N$  is the number of electrons, found by subtracting Table III from Table IV.

$N$	Exact <sup>a</sup>	Extrapolation	MZ <sup>b</sup>	PBE	LYP
2	36.6	36	37	38	34
3		36	38	47	39
7		138	151	161	129
8		199	194	206	184
9		265	237	257	236
10	328.0	332	299	307	286
11		304	311	329	307

<sup>a</sup>References 13 and 14.

<sup>b</sup>Reference 34.

a Hartree–Fock calculation, by virtue of the virial theorem,<sup>40</sup>  $T^{\text{HF}} = -E^{\text{HF}} \approx T_s$ , where  $T^{\text{HF}}$  and  $E^{\text{HF}}$  are the Hartree–Fock kinetic and total electronic energies. Thus knowledge of  $E^{\text{HF}}(Z)$ , for fixed  $N$ , as reported by Davidson *et al.* allows us to estimate  $\gamma(Z)$  for a given neutral, and Eq. (20) then yields  $T_c$ . Figure 6 shows  $E_c[n_\gamma]$  estimated in this way for  $N=10$ . Note that, for example, the  $\gamma \rightarrow \infty$  value differs from  $E_c^{(2)}$  as this curve approximates  $E_c[n_\gamma]$  for the neutral atom density. Lastly, in the spirit of Table III, we use the slope as  $\gamma \rightarrow \infty$  to estimate  $E_c + T_c$  from Eq. (20). Clearly, at  $\gamma=1$ , the density changes are too great to be accurately estimated by our crude approximation.

There is interesting structure in the  $E_c + T_c$  data. In particular, extrapolation values in Table IV show a jump in the magnitude of the correlation energy sum when an electron is placed in a new shell in going from He to Li and from Ne to Na. In contrast, filling the  $p$  orbitals does not appear to be costly. While there is an increase in order of magnitude of correlation, the energy levels off as this subshell is being filled. Trends in the MZ data are different; there are no marked increases in filling a new shell or subshell.

Table V was constructed by subtracting  $E_c$  from Table IV, and shows that extrapolation from the high-density limit yields the best estimates of  $T_c$ .

Table VI shows the performance of the PBE and Lee–Yang–Parr (LYP) correlation functionals in the high-density limit. PW91 and LDA do not behave correctly in this limit and have been excluded from our study. LYP correlation has

TABLE VI. Correlation energy coefficients of  $1/Z$  expansion for select exchange–correlation functionals in milliHartrees, where  $N$  is the number of electrons. Exact number obtained by fitting data in the literature (Refs. 10 and 11.)

$N$	Method	$E_c^{(2)}$	$E_c^{(3)}$	$E_c^{(4)}$
2	LYP	-55.1	1076	-90 276
	PBE	-48.4	5.1	15
	Exact	-46.7	10.0	-1.4
3	LYP	-99	221	-383
	PBE	-59	2.4	58
	Exact	-54	25	1
10	LYP	-524	2733	-77 818
	PBE	-459	623	4 424
	Exact	-428	601	-1 423

greater structure as a function of  $1/Z$ , and so its coefficients are less reliable than the others. The PBE functional behaves better in this limit, although there is much room for improvement. More accurate  $E_c^{(2)}$  values have already been published for a number of ions.<sup>36,31</sup>

While this work was being written, we learned of the work of Staroverov *et al.*,<sup>41</sup> who showed that two conditions must be satisfied for a functional to accurately reproduce the total energy in this limit.<sup>41</sup> The first is that the functional must accurately predict the leading term in the  $Z$  expansion of the exchange energy and the second is that the correlation energy predicted by the functional must scale properly in the high-density limit according to Eq. (2). Their paper reports the behavior of a number of functionals in this limit.

## ACKNOWLEDGMENTS

The authors thank Staroverov *et al.* for sharing their results prior to publication. This work was funded by the National Science Foundation under Grant No. CHE-0355405.

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