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ABSTRACT

Parr and Ghosh [Phys. Rev. A. **51** 3564 (1995)] demonstrated that when near-exact electron densities and potentials are used, the exchange–correlation energies of first- and second-row atoms are well-described by a combination of the Fermi–Amaldi functional with a functional that is homogeneous of degree one under density scaling. Insight into this observation is provided by considering their work from the perspective of the effective homogeneity of the overall exchange–correlation functional. By considering a general form that combines the Fermi–Amaldi functional with a functional that is homogeneous of degree k, it is shown that for these atoms, the functional of Parr and Ghosh ($k = 1$) exhibits essentially optimal effective homogeneities on the electron-deficient side of the integer. Percentage errors in effective homogeneities are close to percentage errors in exchange–correlation energies.

I. INTRODUCTION

Scaling relationships provide key insight into the energy components in density functional theory (DFT). The most commonly encountered scaling is coordinate scaling,[1] where the electronic coordinate is scaled while preserving the electron number. The present study instead focuses on density scaling,[2–5] where the electron density ρ is scaled and the electron number is not preserved. Specifically, a functional, $F[\rho]$, is said to be homogeneous of degree k under density scaling if it satisfies

$$F[\lambda\rho] = \lambda^k F[\rho], \qquad (1)$$

which implies that (for $k \neq 0$)

$$k = \frac{\int \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) d\mathbf{r}}{F[\rho]}. \qquad (2)$$

For example, the Dirac exchange and Thomas–Fermi kinetic energy functionals are homogeneous of degree 4/3 and 5/3, respectively. The density scaling behavior of kinetic energy functionals has attracted particular interest.[6–10]

Evaluation of the quantity k in Eq. (2) can be used to quantify the behavior of any density functional under density scaling. If k is system-independent, then the functional is homogeneous of degree k. If k is system-dependent, then the functional is inhomogeneous and the degree of system dependence provides a measure of the degree of inhomogeneity; in this case, k is usually termed as an *effective* homogeneity[2] and we shall follow this convention. A knowledge of effective homogeneities can, therefore, provide new insight into density functionals, which can be used in the development of new approximations. For example, we have calculated[9] near-exact effective homogeneities for the exchange–correlation and non-interacting kinetic energy functionals and used them to determine new functionals[11–13] and a new approach for estimating negative electron affinities.[14] We have also used homogeneity considerations to derive new approximations[15,16] for use in direct energy Kohn–Sham theory,[17] where the electronic energy equals the sum of the orbital energies.

Homogeneity under density scaling also played a key role in the work of Parr and Ghosh in Ref. 18. They used the Zhao–Morrison–Parr (ZMP)[2] procedure to determine near-exact exchange–correlation potentials from near-exact configuration interaction densities, ρ_0, for the atoms He–Ar, partitioning them as

$$v_{xc}(\mathbf{r}) = -\frac{v_J(\mathbf{r})}{N} + v_C(\mathbf{r}). \tag{3}$$

Here, the first term is the Fermi–Amaldi[19] potential of the density ρ_0, which is the ratio of its Hartree potential and the electron number, and it provides a simple mechanism for ensuring the correct asymptotic potential and exchange–correlation hole normalization. The second term, $v_C(\mathbf{r})$, was termed as the constraint potential. Parr and Ghosh wrote the exchange–correlation energy functional as

$$E_{xc}[\rho] = -\frac{J[\rho]}{N} + G_{xc}[\rho], \tag{4}$$

where the first term is the Fermi–Amaldi functional, involving the Hartree functional, $J[\rho]$; the functional derivative of this Fermi–Amaldi functional (treating N as a parameter rather than a functional[20]), evaluated using ρ_0, is the first term in Eq. (3). The quantity $G_{xc}[\rho]$ in Eq. (4) is an unknown functional whose functional derivative, evaluated using ρ_0, is the constraint potential in Eq. (3),

$$\left.\frac{\delta G_{xc}[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_0} = v_C(\mathbf{r}). \tag{5}$$

The problem is that there are many $G_{xc}[\rho]$ that satisfy Eq. (5). Parr and Ghosh made the approximation that $G_{xc}[\rho]$ is homogeneous of degree one under density scaling, from which Eqs. (2) and (5) yield

$$G_{xc}[\rho_0] = \int v_C(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}. \tag{6}$$

It also follows that the total electronic energy reduces to the sum of the orbital energies minus the Hartree/Fermi–Amaldi energy, meaning that it can be evaluated directly from a knowledge of the density and external potential, which was an objective of Parr and Ghosh. See Refs. 21 and 22 for related work. See also Ref. 23 for a recent derivation and reinterpretation of the Fermi–Amaldi functional.

A key finding of Parr and Ghosh was that the evaluation of Eq. (4), using ρ_0, together with Eq. (6), led to good-quality exchange–correlation and total electronic energies for the atoms considered. The aim of the present study is to provide insight into their observations by considering their work from the perspective of the effective homogeneity of the *overall* exchange–correlation functional in Eq. (4). Specifically, we consider a more general approximation where $G_{xc}[\rho]$ is homogeneous of some arbitrary degree, k, and quantify how the accuracy of the effective homogeneity of the exchange–correlation functional depends on k. We also consider the relationship between the accuracy of the effective homogeneity and the accuracy of the exchange–correlation energy.

II. METHODOLOGY AND RESULTS

We start by defining the near-exact exchange–correlation potential in the same manner as Parr and Ghosh, namely in Eq. (3). Next, we define the exchange–correlation energy functional in the same manner as Eq. (4) but with an additional superscript, k, because

we now approximate the unknown $G_{xc}[\rho]$ to be homogenous of degree k under density scaling,

$$E_{xc}^k[\rho] = -\frac{J[\rho]}{N} + G_{xc}^k[\rho], \tag{7}$$

where, as before,

$$\left.\frac{\delta G_{xc}^k[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_0} = v_C(\mathbf{r}). \tag{8}$$

Given that $G_{xc}^k[\rho]$ is homogeneous of degree k, it follows from Eq. (2) that

$$G_{xc}^k[\rho_0] = \frac{1}{k} \int v_C(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}. \tag{9}$$

From Eq. (2), we now introduce the central quantity of this study, namely the effective homogeneity (Ref. 2) of $E_{xc}^k[\rho]$, evaluated using ρ_0,

$$k_{xc}^k = \frac{\int v_{xc}(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}}{E_{xc}^k[\rho_0]}, \tag{10}$$

where we have used the fact that the functional derivative of $E_{xc}^k[\rho]$, evaluated using ρ_0, is the near-exact potential in Eq. (3), for all values of k. Using Eqs. (3), (7), and (9), together with the fact that the Hartree functional is homogeneous of degree two under density scaling, Eq. (10) reduces to

$$k_{xc}^k = \frac{-\frac{2J[\rho_0]}{N} + kG_{xc}^k[\rho_0]}{E_{xc}^k[\rho_0]} = \frac{-\frac{2J[\rho_0]}{N} + kG_{xc}^k[\rho_0]}{-\frac{J[\rho_0]}{N} + G_{xc}^k[\rho_0]}. \tag{11}$$

We have evaluated k_{xc}^k in Eq. (11) for the atoms He–Ar using the near-exact Hartree energies of Ref. 24. The evaluation of k_{xc}^k also requires the values of $G_{xc}^k[\rho_0]$. Given that Parr and Ghosh tabulated values of $G_{xc}^1[\rho_0]$ [i.e., Eq. (9) with $k = 1$] for these atoms, it is trivial to evaluate $G_{xc}^k[\rho_0]$ from those data,

$$G_{xc}^k[\rho_0] = \frac{1}{k}G_{xc}^1[\rho_0]. \tag{12}$$

We shall compare k_{xc}^k determined using Eq. (11) with near-exact values, denoted $k_{xc,0}$, from Ref. 9, which provide our best estimates for the effective homogeneity of the exact exchange–correlation functional. These were determined in Ref. 9 by evaluating

$$k_{xc,0} = \frac{\int v_{xc}(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}}{E_{xc,0}[\rho_0]} \tag{13}$$

using near-exact ZMP exchange–correlation potentials, electron densities, and exchange–correlation energies. Reference 9 did not consider He, Ne, or Ar, but the $k_{xc,0}$ values for these atoms are easily calculated using the data in Ref. 24. Following Refs. 9 and 25, we omit the Si atom.

As noted in Ref. 9, the effective homogeneity is affected by the integer discontinuity[26] in the exact exchange–correlation potential. Given that Eqs. (10) and (13) are both evaluated using the asymptotically vanishing ZMP potential [Eq. (3)], which is appropriate for the
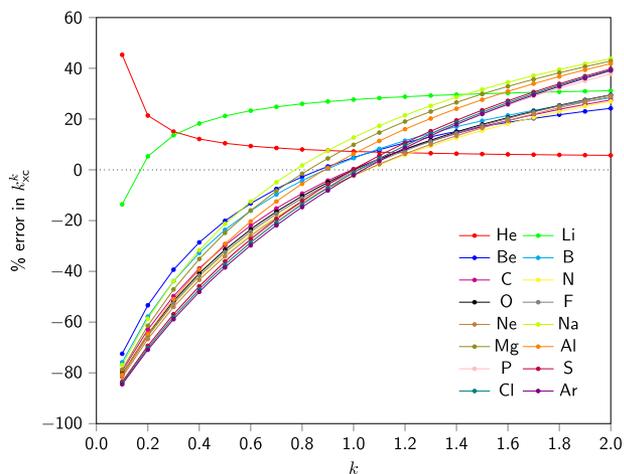
FIG. 1. Percentage errors in k_{xc}^k, as a function of k, for the atoms listed.
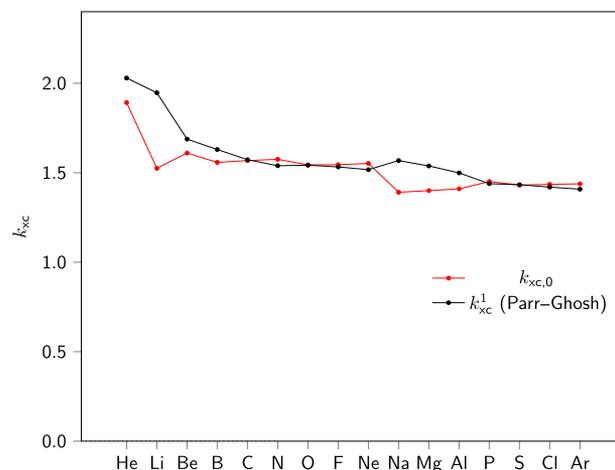
FIG. 3. Values of $k_{xc,0}$ and k_{xc}^1 (Parr–Ghosh) for the atoms in Fig. 1.

electron deficient side of the integer, it follows that k_{xc}^k and $k_{xc,0}$ are effective homogeneities on the electron-deficient side of the integer. For further details, see Ref. 9.

Figure 1 presents the percentage errors in k_{xc}^k, relative to $k_{xc,0}$, as a function of k in the range $0.1 \le k \le 2$, with an interval of 0.1. (The percentage error is defined as $100 \times (k_{xc}^k - k_{xc,0})/k_{xc,0}$.) Each curve represents a different atom. The curves for He and Li are outliers. All the others exhibit a similar shape, shifting smoothly from large negative to large positive percentage errors, with increasing k. Therefore, for all but He and Li, a mid-range value of k yields the smallest percentage error. Figure 2 presents the mean percentage and mean absolute percentage errors, averaged over all the atoms. The key observation is that the mean absolute percentage error minimizes at $k = 1$. (We have verified that the errors continue to increase for val-

ues of $k > 2$; the actual minimizing k is just marginally greater than unity.) The approximation made by Parr and Ghosh—that $G_{xc}[\rho]$ is homogeneous of degree one under density scaling—therefore leads to essentially optimal (in the mean absolute percentage sense) effective homogeneities of the overall exchange–correlation functional, from all functionals of the form of Eq. (7), for the atoms considered.
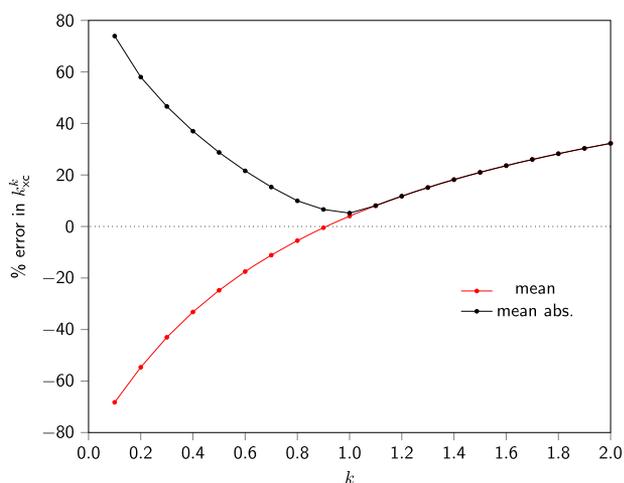
Figure 3 presents the near-exact $k_{xc,0}$ values. They are system-dependent, varying between 1.4 and 1.9, indicating that for these atoms, a functional that yields accurate exchange–correlation energies and the ZMP potential is not approximately homogeneous under density scaling. At first sight, this appears to be at odds with the success of universal local functionals, such as general-ized gradient approximations, which are approximately homoge-neous of degree 4/3 under density scaling due to their dominant Dirac exchange component. However, local functionals do *not* yield potentials that resemble the ZMP potential but, instead, yield poten-tials that approximately average over the integer discontinuity, i.e., they are shifted from the ZMP potential. There is, therefore, no requirement that their effective homogeneities should resemble the system-dependent $k_{xc,0}$ values. See Refs. 9, 25, and 27 for further dis-cussion. By contrast, the functional in Eq. (7) does yield the ZMP potential, and so its effective homogeneities should resemble $k_{xc,0}$. Figure 3 shows that the optimal values, k_{xc}^1, are reasonably close to $k_{xc,0}$, although there is room for improvement. Some periodic struc-ture is evident in the figure, e.g., the behavior of the data for $N \to O \to F \to Ne$ closely resembles that for $P \to S \to Cl \to Ar$, with a good agreement between k_{xc}^1 and $k_{xc,0}$ for all those atoms. The agreement is less good for Li, Be, and B and for Na, Mg, and Al.

Finally, we consider the relationship between errors in the effective homogeneity of the exchange–correlation functional and errors in the exchange–correlation energy. Equations (10) and (13) have the same numerator on the right-hand side, and so

FIG. 2. Mean and mean absolute percentage errors in k_{xc}^k, as a function of k, for the atoms in Fig. 1.

$$k_{xc}^k E_{xc}^k[\rho_0] = k_{xc,0} E_{xc,0}[\rho_0], \qquad (14)$$
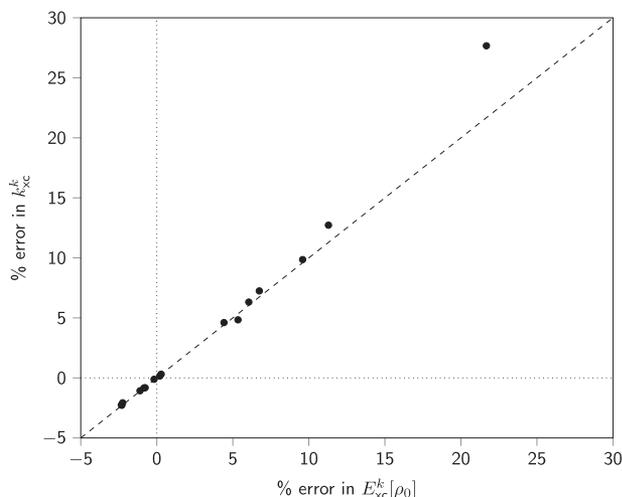
FIG. 4. Scatter plot of percentage errors in k_{xc}^k and percentage errors in $E_{xc}^k[\rho_0]$ for the atoms in Fig. 1.

which yields the result

$$\left(\frac{k_{xc}^k - k_{xc,0}}{k_{xc,0}} \right) = \left(\frac{E_{xc,0}[\rho_0] - E_{xc}^k[\rho_0]}{E_{xc}^k[\rho_0]} \right). \tag{15}$$

The left-hand side of Eq. (15), multiplied by 100, is the percentage error in k_{xc}^k, plotted in Figs. 1 and 2. The right-hand side of Eq. (15), multiplied by 100, is not, however, the percentage error in $E_{xc}^k[\rho_0]$; that would instead require the denominator to be replaced by $E_{xc,0}[\rho_0]$. (Note that the order of the terms in the numerator is reversed compared to the left-hand side because the energy is negative.) It follows that for values of k where the exchange–correlation energy errors are small ($E_{xc}^k[\rho_0] \approx E_{xc,0}[\rho_0]$), the percentage error in k_{xc}^k will be close to the percentage error in $E_{xc}^k[\rho_0]$. This is demonstrated in Fig. 4, which plots these percentage errors for Parr and Ghosh's $k = 1$ functional using the exchange–correlation energy data from Refs. 18 and 24.

III. CONCLUSIONS

We have revisited the work of Parr and Ghosh,[18] viewing it from the perspective of the effective homogeneity of the overall exchange–correlation functional. We demonstrated that their key approximation—that $G_{xc}[\rho]$ is homogeneous of degree one under density scaling—leads to essentially optimal effective homogeneities on the electron-deficient side of the integer, from all functionals of the form of Eq. (7), for the atoms considered. We also demonstrated that percentage errors in effective homogeneities are close to percentage errors in exchange–correlation energies. The study provides further evidence for the utility of effective homogeneities in DFT. It also suggests that further investigation of the Parr–Ghosh form may be warranted. We are currently investigating the extent to which these atomic findings are valid for molecular systems.

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AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

David J. Tozer: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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