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Effective homogeneity of the exchange-correlation energy functional

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Following Zhao, Morrison, and Parr [Q. Zhao, R. C. Morrison, and R. G. Parr. Phys. Rev. A **50**, 2138 (1994)], we examine the effective homogeneity of the exact exchange-correlation energy functional for a set of open-shell atoms. By explicitly considering the influence of the integer discontinuity in the exact exchange-correlation potential, our results suggest that on the limiting electron deficient and electron abundant sides of the integer, the exact functional is poorly represented by any functional that is approximately homogeneous in the electron density. In contrast, a functional whose potential averages over the exact discontinuity must be approximately homogeneous of degree 4/3 in the density, and this is particularly so for the heavier atoms. This observation supports the view that continuum functionals, dominated by local density exchange, must exhibit such an average behavior. The asymptotic breakdown of this average behavior in conventional continuum functionals has important consequences for the computation of long-range properties.
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I. INTRODUCTION

It is now possible to compute routinely (within an additive constant) accurate exchange-correlation potentials for atoms and small molecules from high quality *ab initio* electron densities [1–3]. These potentials provide an important insight into Kohn-Sham density functional theory (DFT) [4,5], and the aim of this study is use them to investigate homogeneity properties of the exact exchange-correlation energy functional. Following an earlier study by Zhao *et al.* [1], we use an ''effective homogeneity parameter'' to quantify our results, and place particular emphasis on how this quantity is influenced by the integer discontinuity in the exact exchange-correlation potential. In Sec. II we discuss this discontinuity and write down simple expressions for the exact potential in open-shell systems. In Sec. III we use approximations to these potentials to examine the effective homogeneity of the exact functional for first- and second-row atoms, and in Sec. IV we relate our observations to the behavior and performance of popular exchange-correlation functionals. Conclusions are presented in Sec. V.

II. EXCHANGE-CORRELATION POTENTIALS

Perdew *et al.* [6] have demonstrated that a plot of the exact energy of a system, as a function of the number of electrons, consists of a series of straight line segments connecting adjacent integers. By definition, the slopes of the segments on the electron deficient and electron abundant sides of the integer N are equal to $-I$ and $-A$, respectively, where I and A are the ionization potential and electron affinity of the N-electron system. Within the Kohn-Sham formalism, these derivative discontinuities manifest themselves as integer discontinuities in the exact exchange-correlation potential—i.e., the exact potential must jump discontinuously as the number of electrons increases through an integer [6]. Exchange-correlation potentials computed from electron densities, such as the ''ZMP potentials'' $v_{\mathrm{ZMP}}(\mathbf{r})$ of Zhao *et al.* [1], vanish asymptotically by construction. In the limit of an exact density, the ZMP potential may therefore be identified as the electron deficient limit of the exact exchange-correlation potential [7]. For open-shell systems within a restricted formalism (i.e., $\epsilon_N = \epsilon_{N+1}$), the discontinuity in the potential equals the discontinuity in the slope of the energy, and so the electron abundant limit of the exact potential is shifted at all points in space from the electron-deficient limit by $(I-A)$ [6,7]. (The situation is more complicated for closed-shell systems due to an additional kinetic contribution to the shift, arising from the occupation of a new Kohn-Sham orbital.) For open-shell systems, the exact limiting exchange-correlation potentials may therefore be conveniently expressed in terms of the exact ZMP potentials

$$v_{\mathrm{xc}}(\mathbf{r})|_{N-\delta} = v_{\mathrm{ZMP}}(\mathbf{r}), \tag{1}$$

$$v_{\mathrm{xc}}(\mathbf{r})|_{N+\delta} = v_{\mathrm{ZMP}}(\mathbf{r}) + (I-A). \tag{2}$$

III. EFFECTIVE HOMOGENEITY FOR OPEN-SHELL ATOMS

A functional $A[\rho]$ is homogeneous of degree k in the electron density if, for all densities $\rho(\mathbf{r})$, it satisfies

$$kA[\rho] = \int \frac{\delta A[\rho]}{\delta \rho(\mathbf{r})} \rho(\mathbf{r}) d\mathbf{r}. \tag{3}$$

Based on this definition, Zhao *et al.* [1] have defined an ''effective homogeneity parameter'' for the exact exchange-correlation functional

$$k_{\mathrm{eff}} = \frac{1}{E_{\mathrm{xc}}[\rho]} \int v_{\mathrm{xc}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}. \tag{4}$$

The degree to which this quantity is system independent is a measure of the degree to which the exact functional is homogeneous in the density. Zhao *et al.* evaluated effective homogeneities for He, Be, Ne, and Ar, using accurate densities and exchange-correlation energies, together with the as-

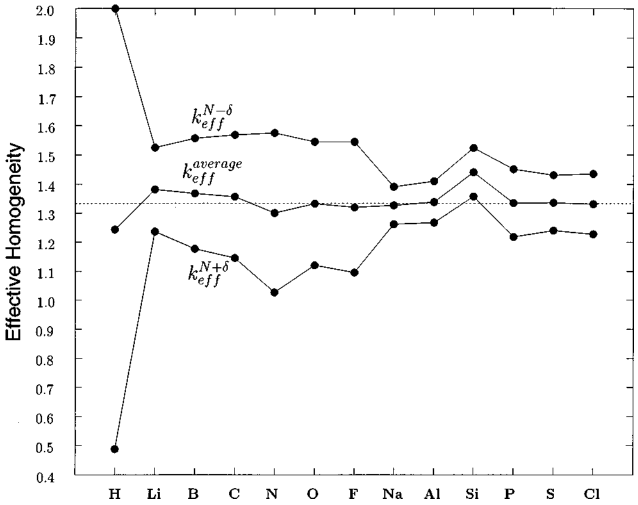

FIG. 1. The effective homogeneities $k_{\mathrm{eff}}^{N\pm\delta}$ [Eqs. (5) and (6)] and $k_{\mathrm{eff}}^{\mathrm{average}}$ [Eq. (7)] for the first- and second-row open-shell atoms, computed using the data in [8] and [9].

sumption $v_{\mathrm{xc}}(\mathbf{r})=v_{\mathrm{ZMP}}(\mathbf{r})$. From Eq. (1), their calculations were therefore implicitly on the electron-deficient side of the integer. We generalize their analysis to examine the effective homogeneity on both the electron-deficient and electron-abundant sides of the integer. Substituting Eqs. (1) and (2) into Eq. (4) we obtain the open-shell result

$$k_{\mathrm{eff}}^{N-\delta}=\frac{1}{E_{\mathrm{xc}}[\rho]}\int v_{\mathrm{ZMP}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \tag{5}$$

$$k_{\mathrm{eff}}^{N+\delta}=\frac{1}{E_{\mathrm{xc}}[\rho]}\int v_{\mathrm{ZMP}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}+\frac{N(I-A)}{E_{\mathrm{xc}}[\rho]}. \tag{6}$$

For a given system, these values indicate the effective homogeneity that the exact functional must exhibit if accurate energies and densities are to be obtained in association with the potentials in Eqs. (1) and (2). Approximations to the integrals and exchange-correlation energies on the right-hand side of Eqs. (5) and (6) have been computed by Morrison and Zhao [8], using CI densities, for the first- and second-row open-shell atoms. They do not present results for the H atom, although since the ZMP potential for this atom is the negative of the Hartree potential, and $E_{\mathrm{xc}}[\rho]$ is the negative of the Hartree energy, we trivially obtain $k_{\mathrm{eff}}^{N-\delta}=2.0$. Values of $(I-A)$ for all the atoms are presented in Ref. [9]. We have computed values of $k_{\mathrm{eff}}^{N\pm\delta}$ using these data, and present the results in Fig. 1.

It is clear that both $k_{\mathrm{eff}}^{N-\delta}$ and $k_{\mathrm{eff}}^{N+\delta}$ are highly system dependent. This indicates that for these atoms, the exact functional cannot be well represented on the limiting electron-deficient or electron-abundant sides of the integer by any functional that is approximately homogeneous in the density. Zhao *et al.* made an equivalent observation in their electron-deficient study of the closed-shell atoms He, Be, Ne, and Ar [1]. We observe that the value of $k_{\mathrm{eff}}^{N-\delta}$ for the Si atom appears anomalous. While the value of $k_{\mathrm{eff}}^{N-\delta}$ increases approximately linearly from $B\rightarrow C\rightarrow N$, the analogous behavior for Al→Si→P is very different. We also note that Si is one of the two atoms for which Parr and Ghosh [10] have presented different exchange-correlation energies to Morrison and Zhao.

In Fig. 1 we also present values of the quantity

$$k_{\mathrm{eff}}^{\mathrm{average}}=\tfrac{1}{2}[k_{\mathrm{eff}}^{N+\delta}+k_{\mathrm{eff}}^{N-\delta}], \tag{7}$$

which represents the effective homogeneity of a functional that gives the exact energy, and a potential for integer N that *averages* over the exact discontinuity, i.e.,

$$v_{\mathrm{xc}}(\mathbf{r})|_{\mathrm{average}}=\tfrac{1}{2}[v_{\mathrm{xc}}(\mathbf{r})|_{N-\delta}+v_{\mathrm{xc}}(\mathbf{r})|_{N+\delta}] \tag{8}$$

or

$$v_{\mathrm{xc}}(\mathbf{r})|_{\mathrm{average}}=v_{\mathrm{ZMP}}(\mathbf{r})+\frac{(I-A)}{2}. \tag{9}$$

The dotted line in Fig. 1 corresponds to $k_{\mathrm{eff}}=4/3$. For the atoms H to F, the values of $k_{\mathrm{eff}}^{\mathrm{average}}$ are reasonably close to 4/3, particularly for the heavier atoms. For the second-row atoms, the values for Na, Al, P, S, and Cl are strikingly close to 4/3. We also observe that if the value of $k_{\mathrm{eff}}^{N-\delta}$ for Si is lowered such that there is an approximately linear increase from Al to P—as is the case for the first row—then the value of $k_{\mathrm{eff}}^{\mathrm{average}}$ is also very close to 4/3. Further investigation is required to resolve this discrepancy with Si. However, excluding this atom, the results of Fig. 1 indicate that for these open-shell atoms, a functional whose potential averages over the exact discontinuity must be approximately homogeneous of degree 4/3 if it is to yield accurate energies. This is a particularly good approximation for the heavier atoms.

IV. RELATION TO CONTINUUM FUNCTIONALS

Conventional local or GGA-type functionals such as LDA [11], BLYP [12], and PW91 [13] are continuum functionals. Their potentials do not exhibit integer discontinuities, and it has previously been argued that such functionals should therefore give potentials that average over the discontinuity in the exact potential [14–16]. (The situation is more complicated for functionals involving a fraction of exact orbital exchange [17].) The results of the previous section support this requirement of an average behavior. Continuum functionals are dominated by exchange, whose major contribution is the local density term $C_x\int\rho^{4/3}(\mathbf{r})d\mathbf{r}$. This is exactly homogeneous of degree 4/3 in the density, and so continuum functionals are also approximately homogeneous of degree 4/3. Figure 1 shows that for the open-shell atoms, any functional that is approximately homogeneous of degree 4/3 can only yield accurate energetics and densities if its potential approximately averages over the discontinuity.

Our previous studies [7,18,19] on both closed- and open-shell systems also support the requirement of such average behavior. In the general case, the potential that averages over the discontinuity (in a restricted formalism) may be written as [7]

$$v_{\mathrm{xc}}(\mathbf{r})|_{\mathrm{average}}=v_{\mathrm{ZMP}}(\mathbf{r})+v_{\mathrm{xc}}^{\infty},\quad v_{\mathrm{xc}}^{\infty}\leqslant\frac{(I-A)}{2}, \tag{10}$$

where the equality holds for open-shell systems, thereby giving Eq. (9). We have written down flexible continuum functional forms and have varied the parameters such that both energies and densities are computed accurately for a chosen set of atoms and molecules. The resulting functionals yield potentials that are consistent with Eq. (10) [7]. Such studies also allow us to compute effective homogeneities for closed-shell systems, since we use the required restricted formalism for these systems. Our calculations imply that accurate continuum exchange-correlation potentials for the closed-shell atoms He, Be, Ne, and Mg are given by Eq. (10) with $v_{\mathrm{xc}}^{\infty}=8.5$, 5.4, 7.5, and 1.8 eV, respectively. The corresponding effective homogeneities computed using the potentials and energies of Morrison and Zhao are 1.31, 1.31, 1.33, and 1.34, respectively. As for the open-shell atoms in Fig. 1, this is much less system dependent than the corresponding electron-deficient effective homogeneities of 1.89, 1.60, 1.55, and 1.39 (the first three of which are equivalent to the values obtained by Zhao *et al.* [1]).

In summary, the results of Fig. 1, together with our previous studies, support the requirement that a quality continuum functional must yield a potential that averages over the discontinuity in the exact potential, i.e., it must give a potential of the form (10). How well do conventional continuum functionals such as LDA, BLYP, and PW91 satisfy this requirement? In energetically important regions (i.e., core/valence) such continuum potentials do closely resemble Eq. (10) [20]. Specific examples have been presented [7,18,21], although this feature is most evident from the highest occupied Kohn-Sham eigenvalues. The highest occupied orbital (HOMO) is relatively localized, and so its eigenvalue is primarily determined by the potential in energetically important regions [7]. If the continuum potential resembled $v_{\mathrm{ZMP}}(\mathbf{r})$ in these regions then the HOMO eigenvalue would be near $-I$ [1]. However, continuum HOMO eigenvalues are much higher than $-I$, being near $-(I+A)/2$ for open-shell systems [14]. This discrepancy indicates that the continuum potential is shifted from $v_{\mathrm{ZMP}}(\mathbf{r})$ in energetically important regions (by approximately $-(I+A)/2-(-I)=(I-A)/2$ for open shells) and so closely resembles Eq. (10).

Next consider asymptotic regions. In these regions the potential in Eq. (10) behaves like $-1/r+v_{\mathrm{xc}}^{\infty}$. The potentials of conventional continuum functionals do *not* behave in this manner. They vanish asymptotically. This breakdown in the average behavior represents a fundamental deficiency in conventional functionals, which is related to the fact that such functionals are determined with an emphasis on accurate energies, for which there is little contribution from asymptotic regions. Because the potentials of conventional continuum functionals are reasonably accurate in energetically important regions, but significantly in error in asymptotic regions, the depth of the potential well—i.e., the difference between the bottom of the well and the vacuum level—is too low by the quantity v_{xc}^{∞}, which is typically about 5 eV. Unlike the occupied eigenvalues, the virtual eigenvalues are therefore very poor, with few (if any) being bound. Long-range properties that rely on accurate differences between occupied and virtual eigenvalues, such as polarizabilities [22] and Rydberg excitation energies [23,24], are correspondingly very poor.

Resolving this error in continuum functionals requires modification of the long-range exchange-correlation potential such that it continues to represent the appropriate average behavior (10). Such a change will leave the effective homogeneity relatively unchanged due to the small contribution to Eq. (4) from asymptotic regions. Our procedure [7] for developing new functionals is designed to achieve this goal, although obtaining the precise $-1/r+v_{\mathrm{xc}}^{\infty}$ behavior is very difficult. However, if it can be achieved, continuum functionals should yield improved virtual Kohn-Sham eigenvalues, with an associated improvement in long-range properties. Such functionals will continue to yield highest occupied eigenvalues close to $-(I+A)/2$ for open-shell systems, although the vacuum level, together with most of the bound virtual eigenvalues, will lie at positive energies.

This strategy for improving continuum functionals differs from the frequently stated viewpoint that highest occupied continuum eigenvalues must be made closer to $-I$. Such an approach would require a continuum potential to mimic the ZMP potential, which in turn would require the effective homogeneity of the continuum functional to approach $k_{\mathrm{eff}}^{N-\delta}$. From Fig. 1, together with the corresponding closed-shell discussion, such a continuum functional could no longer be dominated by $C_x\int\rho^{4/3}(\mathbf{r})d\mathbf{r}$, and we have previously presented results demonstrating the dramatic failure of continuum functionals within this framework [25].

V. CONCLUSIONS

In this paper we have used approximate ZMP potentials, from the calculations of Morrison and Zhao [8], to examine the effective homogeneity of the exact exchange-correlation energy functional for open-shell atoms. Particular emphasis has been placed on the influence of the integer discontinuity in the exact potential. No simple homogeneity is observed on the limiting electron deficient or electron abundant sides of the integer. In contrast, the results indicate that any functional whose potential averages over the discontinuity must be approximately homogeneous of degree 4/3 in the density. Conversely, any functional that is approximately homogeneous of degree 4/3 must yield a potential that approximately averages over the exact discontinuity, in line with previous arguments regarding the behavior of continuum functionals [14–16]. We have then gone on to relate the asymptotic breakdown of this feature to known deficiencies in the long-range properties of conventional continuum functionals, and have outlined the improvements that are necessary to overcome these deficiencies. Such improvements offer the possibility of improved long-range properties from Kohn-Sham theory, and we are investigating this area [26].

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[1] Q. Zhao, R. C. Morrison, and R. G. Parr, Phys. Rev. A **50**, 2138 (1994).

[2] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, J. Chem. Phys. **104**, 8535 (1996).

[3] D. J. Tozer, V. E. Ingamells, and N. C. Handy, J. Chem. Phys. **105**, 9200 (1996).

[4] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[5] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[6] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).

[7] D. J. Tozer and N. C. Handy, J. Chem. Phys. **108**, 2545 (1998).

[8] R. C. Morrison and Q. Zhao, Phys. Rev. A **51**, 1980 (1995).

[9] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).

[10] R. G. Parr and S. K. Ghosh, Phys. Rev. A **51**, 3564 (1995).

[11] P. A. M. Dirac, Proc. Cambridge Philos. Soc. **26**, 376 (1930); S. J. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[12] A. D. Becke, Phys. Rev. A **38**, 3098 (1988); C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[13] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[14] J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

[15] J. P. Perdew, in *Density Functional Methods in Physics*, Vol. 123 of NATO Advanced Study Institute Series B: Physics, edited by R. M. Dreizler and J. da Providencia (Plenum, New York, 1985), p. 265.

[16] J. P. Perdew and M. Levy, Phys. Rev. B **56**, 16 021 (1997).

[17] G. K.-L. Chan, J. Chem. Phys. (to be published).

[18] D. J. Tozer and N. C. Handy, J. Phys. Chem. A **102**, 3162 (1998).

[19] N. C. Handy and D. J. Tozer, Mol. Phys. **94**, 707 (1998).

[20] J. P. Perdew and K. Burke, Int. J. Quantum Chem. **57**, 309 (1996).

[21] D. J. Tozer, Phys. Rev. A **56**, 2726 (1997).

[22] S. A. C. McDowell, R. D. Amos, and N. C. Handy, Chem. Phys. Lett. **235**, 1 (1995).

[23] A. Savin, C. J. Umrigar, and X. Gonze, Chem. Phys. Lett. **288**, 391 (1998).

[24] M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, J. Chem. Phys. **108**, 4439 (1998).

[25] D. J. Tozer, N. C. Handy, and W. H. Green, Chem. Phys. Lett. **273**, 183 (1997).

[26] D. J. Tozer and N. C. Handy (unpublished).