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Asymptotic properties of the exchange energy density and the exchange potential of finite systems: relevance for generalized gradient approximations

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Abstract. It is shown that generalized gradient approximations (GGAs) for exchange only, due to their very limited form, quite generally can not simultaneously reproduce both the asymptotic forms of the exchange energy density and the exchange potential of finite systems. Furthermore, mechanisms making GGAs formally approach at least one of these asymptotic forms do not improve the corresponding quantity in the relevant part of the asymptotic regime of atoms. By constructing a GGA which leads to superior atomic exchange energies compared to all GGAs heretofore but does not reproduce the asymptotic form of the exact exchange energy density it is demonstrated that this property is not important for obtaining extremely accurate atomic exchange energies. We conclude that GGAs by their very concept are not suited to reproduce these asymptotic properties of finite systems. As a byproduct of our discussion we present a particularly simple and direct proof of the well known asymptotic structure of the exchange potential of finite spherical systems.

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1. Introduction

Generalized gradient approximations (GGAs) for the exchange energy functional $E_x[n]$ as introduced by Becke [1], Perdew and Wang [2], DePristo and Kress [3] and Vosko and Macdonald [4] though conceptionally rather simple have been shown to reduce the error of the local density approximation (LDA) substantially (see e.g. [5–9]). The concept behind these GGAs is a partial resummation of the complete gradient expansion for $E_x[n]$ including only first gradients of the density $n(\mathbf{r})$. Recently, Becke [10] has put forward a new GGA which, besides leading to the most accurate total exchange energies (E_x's) for neutral atoms heretofore, satisfies an exact condition on the asymptotic form of the exchange energy density $e_x(\mathbf{r})$ of localized systems (see below) [11–13]. Becke argues that this is an important ingredient for constructing an accurate GGA. To the contrary, we shall show that this asymptotic condition is not important for producing accurate total E_x's in two ways: *(i)* By comparison with the exact $e_x(\mathbf{r})$ it will be shown that the GGA proposed in [10] does not reproduce the exact $e_x(\mathbf{r})$ in the relevant region but approaches its asymptotic form in a regime which is completely unimportant for electronic structure calculations. *(ii)* By constructing a new GGA which on average gives even better E_x's than Becke's functional [10] but does not lead to the correct asymptotic form of $e_x(\mathbf{r})$ it is demonstrated directly that the asymptotic form of $e_x(\mathbf{r})$ is unimportant for obtaining accurate E_x's (on the level of Becke's GGA [10]).

It is worth noting that our comparisons are made with the E_x's derived from the Optimized Potential Model (OPM) [14, 15] (called E_x^{OPM}'s in the following, wherever a clear distinction from other definitions is required) which are the most appropriate values for comparison as has been emphasized in recent years [16–19]. As a matter of principle these E_x^{OPM}'s are different from both the E_x^{HF}'s obtained from the single particle wavefunctions of Hartree-Fock (HF) theory (used in (6) below) and the $E_x^{\text{DFT-HF}}$'s calculated from the density functional theory (DFT) definition of $E_x[n]$ based on the HF approximation, i.e. $E_x^{\text{DFT-HF}}[n] \equiv E_{\text{tot}}^{\text{HF}}[n] - T_s[n] - E_{\text{ext}}[n] - E_H[n]$, where $E_{\text{tot}}^{\text{HF}}[n]$ is the total HF energy functional, $T_s[n]$ is the kinetic energy functional of noninteracting particles, $E_{\text{ext}}[n]$ is the external energy contribution and $E_H[n]$ represents the Hartree term. This point has not always been appreciated in the literature although the differences between E_x^{HF}'s and E_x^{OPM}'s (shown in Table 2) are significant since they are of the same magnitude as the errors the best available GGAs produce.

It also has been suggested [10] that Becke's new GGA might satisfy the asymptotic condition on the corresponding exchange potential $v_x(\mathbf{r})$ [15, 20, 21, 22]. It

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has already been noted very recently (see e.g. [23, 24]) that this in fact is not the case but rather a $v_x(\mathbf{r}) \sim c/r^2$ ($r = |\mathbf{r}|$) results from this GGA (for spherically symmetric systems). We shall explain in detail why the mechanism introduced by Becke for satisfying the asymptotic condition on $e_x(\mathbf{r})$ produces an asymptotic $v_x(\mathbf{r}) \sim c/r^2$. From this discussion it will become clear that for a GGA based on first gradients of the density $n(\mathbf{r})$ there is no other mechanism available to reproduce the asymptotic form of $e_x(\mathbf{r})$, i.e. all forms of GGAs reproducing the exact asymptotic $e_x(\mathbf{r})$ necessarily have the same asymptotic $v_x(\mathbf{r})$. Thus this demonstrates quite generally that GGAs can not satisfy both the asymptotic conditions on $e_x(\mathbf{r})$ and $v_x(\mathbf{r})$ simultaneously. Furthermore we consider a construction in the spirit of Becke's method which reproduces the exact asymptotic behaviour of $v_x(\mathbf{r})$ and show that the underlying mechanism distorts the quality of the GGA in more important regimes of atoms, again indicating the artificial nature of such constructions. We also investigate whether the asymptotic $v_x(\mathbf{r}) \sim c/r^2$ of Becke's new GGA is an improvement over previous v_x^{GGA}'s which decay exponentially, thus elaborating the corresponding remark in [23].

The paper is organized as follows: in Sect. 2 we briefly introduce the concept of the OPM and give a direct and simple DFT proof for the asymptotic form of $v_x(\mathbf{r})$ for finite spherical systems. In Sect. 3 we compare the asymptotic forms of the exact $e_x(r)$ and $v_x(r)$ with those of Becke's new GGA and demonstrate analytically the incompatibility of an asymptotically correct $e_x(\mathbf{r})$ from a GGA with an asymptotically correct $v_x(\mathbf{r})$. We furthermore investigate the construction of a GGA which leads to the correct asymptotic form of $v_x(\mathbf{r})$. Finally, in Sect. 4, we present a simple new GGA which gives superior E_x's without satisfying the asymptotic condition on $e_x(\mathbf{r})$.

2. Theory

Recently, in the context of DFT there has been more emphasis on the asymptotic properties of the exchange energy density $e_x(\mathbf{r})$ and the exchange potential $v_x(\mathbf{r})$ [13, 20, 22, 25, 26]. In this section we briefly review the underlying theory and give a simple proof for the asymptotic form of $v_x(r)$ for finite spherical systems based directly on its DFT definition.

In DFT the contemporary definition of $E_x[n]$ [16–19] (sometimes called exchange only) utilizes the wavefunctions ϕ_i of the so-called OPM [14, 15]. The ϕ_i are those ground state solutions of the OPM equation (in atomic units),

$$\left\{-\frac{\nabla^2}{2}+v_{\mathrm{OPM}}(\mathbf{r})\right\}\phi_i(\mathbf{r})=\varepsilon_i\,\phi_i(\mathbf{r}), \tag{1}$$

with a local potential v_{OPM}, which at the same time minimize the HF energy. Thus the minimization procedure determines both the local v_{OPM} and the corresponding solutions ϕ_i. The exchange energy is then defined using the standard Fock expression with these ϕ_i,

$$E_x[n] = -\tfrac{1}{4}\int \mathrm{d}^3 r \int \mathrm{d}^3 r' \frac{\rho(\mathbf{r},\mathbf{r}')\,\rho(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \tag{2}$$

$$\rho(\mathbf{r},\mathbf{r}') = 2\sum_i \Theta(\varepsilon_F-\varepsilon_i)\,\phi_i^*(\mathbf{r}')\,\phi_i(\mathbf{r}) \tag{3}$$

$$n(\mathbf{r}) \quad = \rho(\mathbf{r},\mathbf{r}), \tag{4}$$

where we have restricted ourselves to spin-saturated systems for simplicity. Applying the Hohenberg-Kohn theorem [27] for noninteracting systems one concludes that v_{OPM} and $E_{\mathrm{HF}}[\phi_i]$ are functionals of the density $n(\mathbf{r})$. Then it follows that (to within a constant)

$$v_{\mathrm{OPM}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_x(\mathbf{r}),$$

where v_{ext} and v_H are the external and Hartree potentials, respectively, and

$$v_x(\mathbf{r}) = \frac{\delta E_x[n]}{\delta n(\mathbf{r})}, \tag{5}$$

with E_x given by (2). Talman and Shadwick [15] (using the integral equation that $v_x(\mathbf{r})$ satisfies) and others [20–22] have shown that for localized systems $v_x(\mathbf{r})$ has the asymptotic form

$$v_x(\mathbf{r}) \xrightarrow[r\to\infty]{} -\frac{1}{r}. \tag{6}$$

Consequently any DFT representation of $E_x[n]$ should aim at satisfying the asymptotic requirement (6) which e.g. is crucial for obtaining accurate eigenvalues for the highest occupied orbital of the Kohn-Sham equations [22, 26, 28, 29].

There is a variety of reasons for choosing this definition of the exchange energy functional in DFT compared to basing $E_x[n]$ on the HF approximation, i.e. using $E_x^{\mathrm{DFT-HF}}[n] \equiv E_{\mathrm{tot}}^{\mathrm{HF}}[n] - T_s[n] - E_{\mathrm{ext}}[n] - E_H[n]$. First of all, as the definition of exchange only is identical to the lowest order term of an expansion of $E_x^{\mathrm{DFT\text{-}HF}}[n]$ in powers of e^2, it is generally more accessible to all kinds of analyses than the complete $E_x^{\mathrm{DFT-HF}}[n]$. In particular, the gradient coefficient of exchange only (for a more detailed discussion see Sect. 3) is known. Also, in contrast to $E_x^{\mathrm{DFT-HF}}[n]$, the definition of exchange only leads to a functional with unique scaling properties [19, 30]. Finally, it allows a direct numerical construction of the corresponding local $v_x(\mathbf{r})$, again offering the possibility of detailed study.

From (2) a possible and natural definition of the exchange energy density is

$$e_x([n];\mathbf{r}) \equiv -\tfrac{1}{4}\int \mathrm{d}^3 r' \frac{\rho(\mathbf{r},\mathbf{r}')\,\rho(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}, \tag{7}$$

which is adopted in this paper (as e.g. in [13]). Gunnarsson and Lundqvist [11] and Levy et al. [12] (in terms of the exchange hole sum rule) as well as March [13] (using the idempotency of the one particle density matrix – a proof which is most useful for our purposes) showed that for localized systems this e_x has the asymptotic structure

$$e_x([n];\mathbf{r}) \xrightarrow[r\to\infty]{} -\frac{n(r)}{2r}. \tag{8}$$

This property of $e_x[n]$ might be of some interest for improving the calculation of energy differences (such as the ionization potential) over the LDA.

At first glance (6, 8) seem to be contradictory: taking the functional derivative (5) of the asymptotic form (8) one ends up with 1/2 of (6). However, it is important to notice that taking the functional derivative does not commute with the limit $r\to\infty$. It is the intrinsic quadratic structure of $E_x[n]$, (2), which restores the missing factor of 2.

To see how this factor of 2 comes about we give a direct DFT proof of (6) on the basis of (5) (which is most easily done for spherically symmetric systems). Our proof is performed in a way so as to parallel March's proof for (8) as much as possible in order to demonstrate the close connection between both asymptotic relations (6) and (8).

For spherical systems the ϕ_i are given by

$$\phi_{nlm}(\mathbf{r}) = \frac{P_{nl}(r)}{r} Y_{lm}(\theta,\varphi) \tag{9}$$

and the density reduces to

$$n(r) = 2\sum_{n,l} \frac{2l+1}{4\pi r^2} (P_{nl}(r))^2 \Theta(\varepsilon_F - \varepsilon_{nl}). \tag{10}$$

For large r one now can replace the functional derivative with respect to $n(\mathbf{r})$ in (5) by a functional derivative with respect to the highest occupied orbital $P_{hk}(r)$,

$$\begin{aligned}\frac{\delta E_x[n]}{\delta n(r)} &= \lim_{\eta\to 0}\frac{1}{\eta}\left\{E\left[n(r')+\eta\frac{\delta(r-r')}{4\pi r^2}\right]-E[n(r')]\right\}\\ &\xrightarrow[r\to\infty]{} \frac{1}{4(2k+1)P_{hk}(r)}\frac{\delta E_x[n]}{\delta P_{hk}(r)},\end{aligned} \tag{11}$$

where we exclude accidental degeneracy for the highest occupied orbital and the δ-function has been normalized with respect to the space in which $n(r)$ is defined. For spherical systems it is straighforward (see e.g. [15]) to express E_x in terms of the $P_{nl}(r)$,

$$\begin{aligned}E_x = -\sum_{n,l}\sum_{n',l'}\Theta(\varepsilon_F-\varepsilon_{nl})\,\Theta(\varepsilon_F-\varepsilon_{n'l'})(2l+1)(2l'+1)\\ \cdot\sum_{L=|l-l'|}^{l+l'} c_{ll'L}\int_0^\infty \mathrm{d}x\int_0^\infty \mathrm{d}y\,\frac{r_<^L}{r_>^{L+1}}\\ \cdot P_{nl}(x)\,P_{n'l'}(x)\,P_{nl}(y)\,P_{n'l'}(y)\end{aligned}$$

where $r_<$ is the smaller of x, y and $r_>$ the larger and

$$\begin{aligned}c_{ll'L} = &\left[\frac{(l'+L-l)!\,(L+l-l')!\,(l+l'-L)!}{(l+l'+L+1)!}\right]\\ &\cdot\left[\frac{\left(\frac{l+l'+L}{2}\right)!}{\left(\frac{l'+L-l}{2}\right)!\left(\frac{L+l-l'}{2}\right)!\left(\frac{l+l'-L}{2}\right)!}\right]^2\end{aligned}$$

if $l+l'+L$ is even and is 0 otherwise. Thus from (11) one obtains

$$\begin{aligned}v_x(r) &\xrightarrow[r\to\infty]{} -\sum_{n,l}\Theta(\varepsilon_F-\varepsilon_{nl})(2l+1)\sum_{L=|l-k|}^{l+k} c_{lkL}\\ &\quad\cdot\left[\frac{P_{nl}(r)}{P_{hk}(r)}\int_0^r \mathrm{d}x\,\frac{x^L}{r^{L+1}}P_{nl}(x)\,P_{hk}(x)\right.\\ &\quad\left.+\frac{P_{nl}(r)}{P_{hk}(r)}\int_r^\infty \mathrm{d}x\,\frac{r^L}{x^{L+1}}P_{nl}(x)\,P_{hk}(x)\right]\\ &\xrightarrow[r\to\infty]{} -\frac{1}{r}\sum_n\Theta(\varepsilon_F-\varepsilon_{nk})(2k+1)\,c_{kk0}\\ &\quad\cdot\frac{P_{nk}(r)}{P_{hk}(r)}\int_0^\infty \mathrm{d}x\,P_{nk}(x)\,P_{hk}(x)\\ &\xrightarrow[r\to\infty]{} -\frac{1}{r},\end{aligned} \tag{12}$$

where the orthonormality of the P_{nl}'s has been used to arrive at (6).

As with all proofs of (6) in the literature, our direct DFT proof relies on the existence of one highest occupied orbital which decays most slowly for large r. Thus the asymptotic form of $v_x(r)$, (6), can only be valid for those r where the total density is well represented by the highest occupied orbital alone. Even more, the norm of the outermost orbital has to integrate almost to 1 as is clear from (12). As March's proof of (8) only uses the idempotency of the density matrix one could at first glance expect the form (8) to become valid for smaller values of r than (6). This impression, however, is misleading as the idempotency of $\rho(\mathbf{r},\mathbf{r}')$ can only be used in (7) after the Coulomb denominator has been replaced by its asymptotic form $1/r$. The r-regime where this replacement is possible is again determined by the highest occupied orbital which defines the finite size of the system. Consequently the r-regime where (6, 8) become valid is identical as can be seen directly from Figs. 1 and 2. Note that both asymptotic forms originate from the same structure in $E_x[n]$ demonstrating their close connection

3. Asymptotic properties of GGAs

The general form of GGAs (for spin saturated systems, using atomic units) is [1–4]

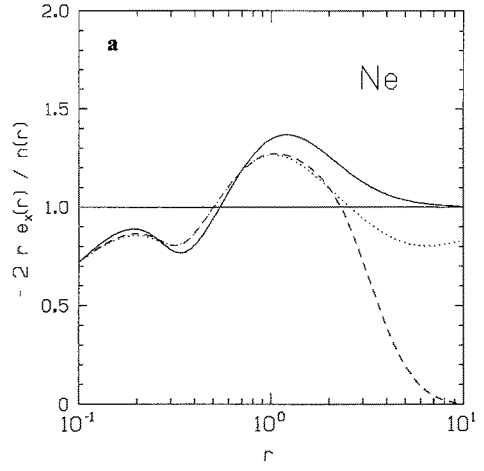
$$E_x^{\mathrm{GGA}}[n] = \int \mathrm{d}^3 r\, e_x^{\mathrm{LDA}}(n) f(\xi), \tag{13}$$

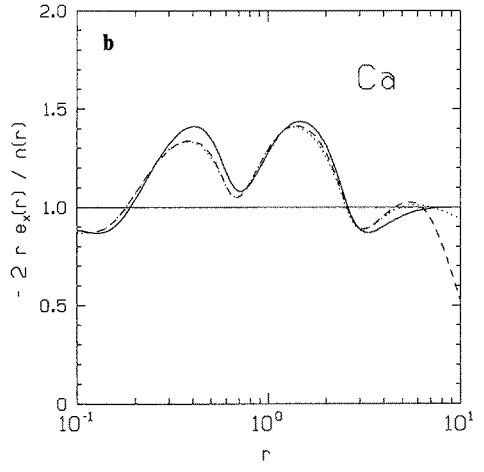
where

$$e_x^{\mathrm{LDA}}(n) = A_x\, n(\mathbf{r})^{\frac{4}{3}}, \qquad A_x = -\frac{3(3\pi^2)^{\frac{1}{3}}}{4\pi} \tag{14}$$

$$\xi(\mathbf{r}) \equiv \left(\frac{\nabla n(\mathbf{r})}{2k_F(\mathbf{r})\,n(\mathbf{r})}\right)^2, \qquad k_F(\mathbf{r}) \equiv (3\pi^2 n(\mathbf{r}))^{\frac{1}{3}}. \tag{15}$$

In order to reduce to the correct limit for a homogeneous system $f(\xi)$ has to approach 1 for vanishing ξ. On the





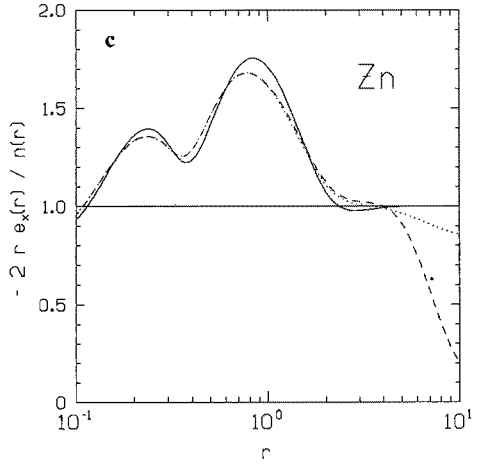
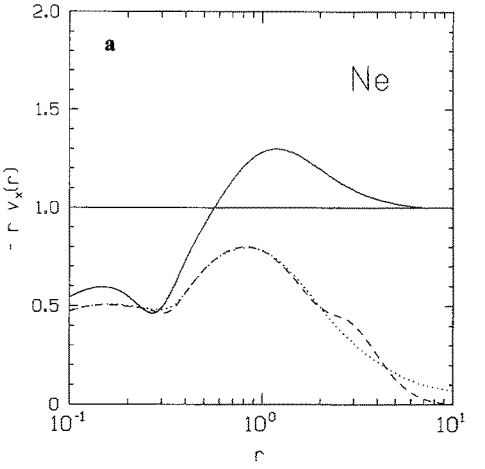
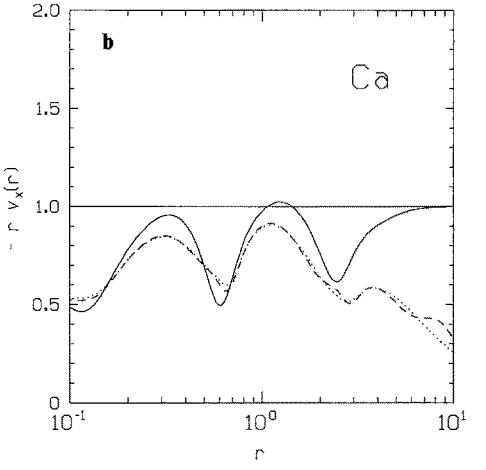


Fig. 1a–c. $-2re_x(r)/n(r)$ for Ne, Ca and Zn: exact – *full line*, GGA (16) – *dotted line*, GGA (23) – *dashed line*





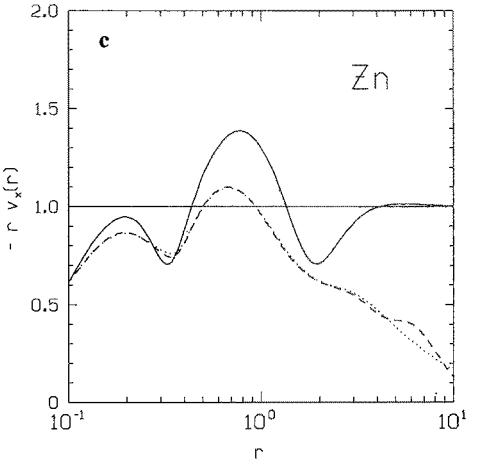


Fig. 2a–c. $-rv_x(r)$ for Ne, Ca and Zn: exact – *full line*, GGA (16) – *dotted line*, GGA (23) – *dashed line*

other hand the prefactor of the lowest order inhomogeneity correction to the LDA as introduced by Herman et al. [31] and Sham [32], though known for weakly inhomogeneous systems from the linear response of the homogeneous electron gas [18, 33], is sometimes viewed as an adjustable parameter, i.e. the constant c_2 in the power series expansion of $f(\xi)$ about $\xi=0$, $f(\xi)=1+c_2\,\xi+\ldots$, is chosen to give optimum exchange energies for neutral atoms [1, 10]. This adjustment leads to a gradient coefficient c_2 that is roughly 2 times larger than that derived from linear response.

Although in contradiction to the linear response result this procedure nevertheless could be appropriate for selfconsistent electronic structure calculations for atoms and molecules analogous to the case of the kinetic energy functional $T_s[n]$: for $T_s[n]$ Lieb [34] has shown by

means of $1/Z$ (nuclear charge) expansion (keeping the ratio N/Z fixed) of the total energy of atoms and molecules that the homogeneous electron gas kinetic energy functional, i.e. the Thomas-Fermi functional, together with a 1.69... times larger gradient correction as obtained from linear response used as an approximate $T_s[n]$ in a selfconsistent calculation reproduce the leading two orders of a $1/Z$ expansion of the exact kinetic energy of these systems. Thus while the dominant contribution to a selfconsistently used $T_s[n]$ of atoms and molecules from the $1/Z$ expansion is identical to the homogeneous electron gas result (in spite of the rather strong inhomogeneity of these systems) the $1/Z$ expansion leads to a larger inhomogeneity correction. This is in contrast to the case of a weakly inhomogeneous system where one would expect the linear response result to give the appropriate gradient coefficient for a selfconsistent calculation. Of course, in most applications of GGAs for $E_x[n]$ the kinetic energy functional is taken into account exactly by using Kohn-Sham equations. However, it might still require a larger gradient coefficient for $E_x[n]$ to reproduce the exchange energy of atoms to the appropriate power of Z by a selfconsistent calculation. In this sense a larger gradient coefficient in GGAs might be justifiable. In any case the value of the gradient coefficient is of little importance for the objective of the present work, i.e. the discussion of the asymptotic properties of GGAs which result from the limit of large gradients.

In contrast to all previous GGAs the functional recently introduced by Becke [10] has been constructed to obey the asymptotic relation (8) for exponentially decaying densities. For spin-saturated systems the proposed GGA has the kernel

$$f_{B88}(\xi)=1-\frac{\beta}{2^{\frac{1}{3}}A_x}\frac{x^2}{1+6\beta x\sinh^{-1}(x)} \tag{16}$$

$$x=2(6\pi^2)^{\frac{1}{3}}\sqrt{\xi}, \tag{17}$$

where $\beta=0.0042$ (a factor of 2.2 larger than the value for β obtained from linear response) has been chosen to reproduce the total HF exchange energies (which are numerically very close to the OPM values – see Table 2) of He and the noble gas atoms. The total exchange energies produced by the functional (16) are so accurate that the form (16) (in particular the $\sinh^{-1}(\xi)$-function) has attracted considerable attention [9, 35, 36]. For an exponentially decaying density (assuming a spherical system) it follows

$$n(r)\xrightarrow[r\to\infty]{} n_0\, r^{\alpha}\,\mathrm{e}^{-\lambda r} \tag{18}$$

$$n'(r)\xrightarrow[r\to\infty]{} -\lambda n(r)\left(1-\frac{\alpha}{\lambda r}+\ldots\right) \tag{19}$$

$$n''(r)\xrightarrow[r\to\infty]{} \lambda^2 n(r)\left(1-\frac{2\alpha}{\lambda r}+\ldots\right) \tag{20}$$

$$\sqrt{\xi(r)}\xrightarrow[r\to\infty]{} \frac{\lambda}{2(3\pi^2 n(r))^{\frac{1}{3}}}\left(1-\frac{\alpha}{\lambda r}+\ldots\right), \tag{21}$$

where n' and n'' are the first and second derivatives of the density with respect to r. Consequently, using (16–18, 21), one finds asymptotically that

$$f_{B88}(\xi)\xrightarrow[r\to\infty]{} -\frac{2(3\pi^2)^{\frac{1}{3}}\xi^{\frac{1}{2}}}{3A_x\ln(\xi)}\xrightarrow[r\to\infty]{} -\frac{1}{2A_x r n(r)^{\frac{1}{3}}} \tag{22}$$

so that $e_x^{B88}([n];\mathbf{r})$ in fact satisfies (8).

It is of interest to examine to what extent the property (8) is actually present in the outer regions of atoms. To investigate this aspect we have calculated $e_x^{\mathrm{OPM}}(r)$, (7), for 15 spherical neutral atoms consisting of 3 major groups behaving similarly in the outer regions: *(i)* alkaline earth – Be, Mg, Ca, Sr, Ba; *(ii)* noble gases – Ne, Ar, Kr, Xe, Rn and *(iii)* Zn, Cd, Hg in which the 2 outermost orbitals are $[np,(n+1)s]$, $[ns,np]$ and $[nd,(n+1)s]$, respectively. We also considered He and Yb (the latter being similar to the alkaline earths). Note that all programs presently available for atomic OPM calculations [15, 37] only allow the exact treatment of spherical systems which is why we restrict ourselves to the atoms listed above. As examples we show $-2re_x(r)/n(r)$ for Ne, Ca and Zn in Fig. 1. Furthermore, we have inserted exact OPM densities [26] into the functional (16) in order to compare its $e_x^{\mathrm{GGA}}(r)$ with $e_x^{\mathrm{OPM}}(r)$ and the results of the GGA initially put forward by Becke [1],

$$f_{B86}(\xi)=1-\frac{\beta}{2^{\frac{1}{3}}A_x}\frac{x^2}{1+\gamma x^2}, \tag{23}$$

(x is given by (17), $\beta=0.0035$, $\gamma=0.004$) chosen as an example of a GGA which leads to an exponentially decaying $e_x([n];r)/n(r)$. It is obvious from Fig. 1 that the functional (16), in contrast to the exact $e_x^{\mathrm{OPM}}(r)$, has not yet approached its asymptotic form at the maximum r-values displayed. On the other hand, in the inner regions there is very little difference between the functionals (16) and (23). It is far beyond ($\sim$2 a.u.) the r-expectation value of the outermost orbital that the two functionals start to become different. The main virtue of the form (16) is that it does not deviate from the exact $e_x(r)$ as much as the form (23) as it approaches the extreme asymptotic regime which contains a neglegible amount of energy.

Even more important than the asymptotic behaviour of $e_x([n];r)$ is that of the corresponding $v_x(r)$. In his paper [10] Becke introduces the Coulomb potential of the exchange hole, which falls off asymptotically like $-1/r$. It is worth noting that this potential is not identical with v_x as the latter quantity is defined as a functional derivative. i.e. by (5). For spherical systems the v_x corresponding to a GGA of the form (13) is given by

$$v_x^{\mathrm{GGA}}(r)=v_x^{\mathrm{LDA}}(n)\cdot\left\{f(\xi)-\frac{3}{2}\frac{1}{4(3\pi^2)^{\frac{2}{3}}}\frac{\mathrm{d}f}{\mathrm{d}\xi}(\xi)\left(\frac{n''}{n^{\frac{5}{3}}}+\frac{2n'}{rn^{\frac{5}{3}}}\right)-\frac{3}{(4(3\pi^2)^{\frac{2}{3}})^2}\frac{\mathrm{d}^2f}{\mathrm{d}\xi^2}(\xi)\frac{(n')^2}{n^{\frac{10}{3}}}\left(\frac{n''}{n}-\frac{4}{3}\frac{(n')^2}{n^2}\right)\right\}. \tag{24}$$

For the following it is useful to note a suitable asymptotic form of this formula,

$$v_x^{\mathrm{GGA}}(r) \xrightarrow[r\to\infty]{} v_x^{\mathrm{LDA}}\left\{ f(\xi) - \frac{3}{2}\xi\left(1-\frac{2}{\lambda r}\right)\frac{\mathrm{d}f}{\mathrm{d}\xi}(\xi) + \xi^2 \frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2}(\xi) + \mathcal{O}\left(\frac{\xi^{\frac{1}{2}}}{r^2 \ln(\xi)}\right)\right\}, \tag{25}$$

where we have replaced the asymptotic n'' and n' in favour of the asymptotic ξ using (18–21). Relative to the leading terms displayed those neglected in (25) are either of order $1/r^2$ or exponentially smaller as ξ increases exponentially for large r. For the functional (16) the asymptotic forms of the required derivatives are

$$\frac{\mathrm{d}}{\mathrm{d}\xi} f_{B88}(\xi) \xrightarrow[r\to\infty]{} -\frac{(3\pi^2)^{\frac{1}{3}}}{3A_x}\frac{1}{\xi^{\frac{1}{2}}\ln(\xi)}\left(1-\frac{2}{\ln(\xi)}\right) \tag{26}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\xi^2} f_{B88}(\xi) \xrightarrow[r\to\infty]{} \frac{(3\pi^2)^{\frac{1}{3}}}{6A_x}\frac{1}{\xi^{\frac{3}{2}}\ln(\xi)}. \tag{27}$$

Again the terms neglected are at least smaller by $1/r^2$ compared to the leading order terms. Insertion into (25) together with (22) then shows that the v_x corresponding to the functional (16) falls off asymptotically as $-5/(2\lambda r^2)$ rather than the required $-1/r$ as all contributions of order $1/r$ cancel out (compare [23, 24]). The asymptotic form of this potential thus depends explicitly on the highest occupied orbital through λ.

This is a general property of Becke's method to construct an $e_x[n]$ that satisfies condition (8): for any GGA this condition can only be satisfied if the kernel $f(\xi)$ behaves asymptotically like (22) (independently of the way in which this asymptotic form is approached, i.e. on the complete form of $f(\xi)$). Consequently the asymptotic forms of the derivatives of $f(\xi)$ are given by (26, 27) and thus the corresponding potential falls off like $-5/(2\lambda r^2)$. It is impossible to satisfy (8) with a GGA only depending on ξ without violating (6) and vice versa.

Since all previous $E_x^{\mathrm{GGA}}[n]$ give rise to v_x's which fall off exponentially in the asymptotic regime of atoms it is interesting to investigate whether the much slower $1/r^2$ decay leads to any improvement (compare the corresponding remark in [23]). In Fig. 2 we have plotted $-r v_x(r)$ obtained by insertion of OPM densities into (24) using the kernel (16) for Ne, Ca and Zn and compare this to the exact $v_x^{\mathrm{OPM}}(r)$ as well as to the GGA (23). For none of the 15 atoms examined is v_x improved in the physically relevant part of the asymptotic regime ($r<10$ a.u.) as the $1/r^2$ behaviour sets in too far outside. Consequently the functional (16) used in a selfconsistent calculation also does not lead to improved highest occupied eigenvalues as can be seen from Table 1.

Table 1. Eigenvalues of highest occupied orbitals (in Hartrees): comparison of exact OPM eigenvalues with the results of (16) and (23) in selfconsistent calculations

Atom	OPM	(16)	(23)
Ne	0.851	0.456	0.455
Ca	0.196	0.116	0.116
Zn	0.293	0.189	0.190

It is interesting to note that the asymptotic form of v_x^{GGA}, (25), suggests a mechanism to generate a potential with the correct asymptotic behaviour. Choosing

$$f(\xi) \xrightarrow[\xi\to\infty]{} c\,\xi^{\frac{1}{2}}$$

one obtains

$$\frac{\mathrm{d}f}{\mathrm{d}\xi}(\xi) \xrightarrow[\xi\to\infty]{} \frac{c}{2}\xi^{-\frac{1}{2}}$$

$$\frac{\mathrm{d}^2 f}{\mathrm{d}\xi^2}(\xi) \xrightarrow[\xi\to\infty]{} -\frac{c}{4}\xi^{-\frac{3}{2}}.$$

Inserting these relations into (25) and using (21) the leading terms cancel out and one ends up with

$$v_x^{\mathrm{GGA}}(r) \xrightarrow[r\to\infty]{} v_x^{\mathrm{LDA}}(n)\frac{3c}{4(3\pi^2 n(r))^{\frac{1}{3}} r}.$$

With

$$c = -\frac{(3\pi^2)^{\frac{1}{3}}}{A_x} \tag{28}$$

one thus can satisfy condition (6). Of course, this asymptotic structure does not satisfy (8). However, given the physically more relevant nature of v_x it might be worth violating (8) if one is able to improve v_x. This is particularly interesting in view of the trend towards using LDA potentials in the calculation of orbitals subsequently inserted into exact expressions for the energy (see e.g. [38]).

In an attempt to implement this idea into a GGA we have tried to optimize the exchange kernel

$$f(\xi) = \left[\frac{1+a_2\,\xi+a_4\,\xi^2+a_6\,\xi^3}{1+b_2\,\xi+b_4\,\xi^2}\right]^{\frac{1}{2}}$$

(and similar forms) restricting a_6/b_4 to satisfy (28) (and fixing a_2-b_2 by the known gradient coefficient from linear response [18, 33] – this restriction has no effect on our conclusions for the asymptotic properties of this functional). We first followed the approach of Vosko and Macdonald [4] to obtain the free coefficients in $f(\xi)$ by fitting the exact $e_x^{\mathrm{OPM}}(r)$ of our 15 neutral spherical atoms. In a second attempt we obtained the free parameters by a direct fit to the exact $v_x^{\mathrm{OPM}}(r)$ of the same set of atoms. In both cases the optimization procedures led to extremely small coefficients a_4, a_6 and b_4 thus effectively switching off the asymptotic $\sqrt{\xi}$ behaviour. Treating both a_6 and b_4 as free parameters in both cases the optimization procedure made a_6 almost vanish. Consequently, as for Becke's mechanism to reproduce the asymptotic $e_x(r)$, these GGAs approach their asymptotic forms for r-values which are completely irrelevant for electronic structure calculations. This indicates that there is no underlying property of the exact $E_x[n]$ behind this artifice to enforce the correct asymptotic behaviour.

4. Accurate GGA violating the asymptotic constraint

In the preceding section we basically have shown that mechanisms making GGAs reproduce either of the asymptotic properties (6) or (8) are not really successful in the sense that the resulting GGAs do not show superior asymptotic behaviour in the physically relevant regime. To demonstrate that the satisfaction of (8) is not required to generate excellent total atomic E_x's we have optimized a [2/2] Padé approximant,

$$f_{[2/2]}(\xi)=\frac{1+a_1\,\xi+a_2\,\xi^2}{1+b_1\,\xi+b_2\,\xi^2}, \tag{29}$$

so as to reproduce the total E_x of the 15 neutral spherical atoms of Sect. 3. As for the GGA (16) we have allowed for a free adjustment of the gradient coefficient. The resulting coefficients are $a_1=27.8428$, $a_2=11.7683$, $b_1=27.5026$, $b_2=5.7728$ (the gradient coefficient resulting from this optimization is about 2.76 times larger than that from linear response). Table 2 shows that this GGA reproduces the E_x's of these atoms on average even slightly better than the functional (16). We have also optimized the GGA (16) by adjusting β to the E_x^{OPM}'s of the specific set of atoms used in our comparison. This led to $\beta=0.0041878$ and an average error of 0.107% which, on this level of accuracy, is still quite different from the error of 0.093% our new GGA generates. This demonstrates indirectly how close to the achievable accuracy both these GGAs actually are. In contrast to the functional (16), however, the GGA (29) does not satisfy (8). It thus is obvious that satisfaction of (8) is not a precondition for obtaining excellent total exchange energies.

Recently, a further criterion for constructing GGAs has been introduced [35] which is based on an exact condition for the exchange energy by Lieb and Oxford [39]. Lieb and Oxford have shown that

$$E_{xc}[n]-T[n]+T_s[n]\geqq c\int \mathrm{d}^3 r\, e_x^{\mathrm{LDA}}(n), \tag{30}$$

where $E_{xc}[n]$ is the exact exchange-correlation functional of DFT, $T[n]$ and $T_s[n]$ are the kinetic energy functionals of the interacting and noninteracting systems, respectively, and the constant $c=2.27$. As $E_x[n]\geqq E_{xc}[n]$ and $T[n]\geqq T_s[n]$ [40, 41] one finds

$$E_x[n]\geqq c\int \mathrm{d}^3 r\, e_x^{\mathrm{LDA}}(n). \tag{31}$$

A sufficient condition for satisfying (31) by a GGA is to construct $f(\xi)$ such that

$$f(\xi)\leqq 2.27, \tag{32}$$

which is equivalent to requiring (31) locally, i.e. for energy densities. In contrast to Becke's GGA (16) our functional (29) does satisfy this criterion. It should be noted, however, that the exact $e_x(r)$ violates this local interpretation of the Lieb-Oxford bound in the asymptotic regime since by (8)

$$e_x(r)=-\frac{n(r)}{2r}\ll 2.27\,A_x\,n(r)^{\frac{4}{3}}=2.27\,e_x^{\mathrm{LDA}}(r)$$

for large r.

5. Concluding remarks

In conclusion we would like to emphasize that in view of our results it seems to be questionable whether the asymptotic conditions discussed in this paper are a reasonable criterion to judge or construct a GGA. All our results indicate that GGAs due to their very limited form are not suited to reproducing these asymptotic properties of finite systems. Mechanisms to enforce these asymptotic properties seem to be artificial and show no success in the relevant part of the asymptotic regime. For practical purposes, which is the main aim of the concept of GGAs, the functionals compared in this work are equivalent with respect to their asymptotic behav-

Table 2. Total E_x^{HF}'s, E_x^{OPM}'s [43] and the deviations of the GGAs (16), (23) and (29) from E_x^{OPM} (in mHartrees) as well as their individual (δ_i) and average absolute ($\bar{\delta}$) percentage errors

Atom	$-E_x^{\mathrm{HF}}$	$-E_x^{\mathrm{OPM}}$	(16)	$\delta_{(16)}$	(23)	$\delta_{(23)}$	(29)	$\delta_{(29)}$
He	1026	1026	−1	−0.142	0	0.031	0	0.000
Be	2667	2666	−3	−0.127	8	0.299	1	0.028
Ne	12108	12105	−57	−0.469	−33	−0.271	−45	−0.369
Mg	15994	15988	−44	−0.278	−12	−0.076	−30	−0.186
Ar	30185	30175	−8	−0.028	21	0.071	8	0.028
Ca	35211	35199	−27	−0.077	7	0.019	−9	−0.025
Zn	69641	69619	−237	−0.341	−248	−0.356	−238	−0.342
Kr	93856	93833	11	0.012	−39	−0.042	−10	−0.011
Sr	101955	101926	26	0.026	−30	−0.029	0	0.000
Cd	148914	148879	74	0.049	−50	−0.034	0	0.000
Xe	179097	179063	199	0.111	21	0.012	94	0.052
Ba	189100	189065	173	0.091	−17	−0.009	57	0.030
Yb	276214	276145	−505	−0.183	−850	−0.308	−737	−0.267
Hg	345304	345244	210	0.061	−247	−0.071	−118	−0.034
Rn	387504	387450	496	0.128	−35	−0.009	109	0.028
$\bar{\delta}$				0.142		0.109		0.093

iour. Our analysis demonstrates that it is necessary to resort to more complicated forms for the exchange energy functional, as e.g. discussed by Ou-Yang and Levy [42], if one wants to make real progress towards improving the asymptotic structure of $E_x[n]$. Also, it appears to be mandatory to consider the conditions (6) and (8) together rather than as separate requirements as they have the same origin in the exact $E_x[n]$. In order to make any improvements for GGAs, however, it seems advisable to concentrate on those regimes in atoms or molecules (and also solids) where GGAs have the potential to approximate the exact $v_x(r)$.

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