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Local exchange-correlation energy density functional for monotonically decaying spherical densities[☆]

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Abstract

Local exchange-correlation functionals are defined for different systems with spherical symmetry, by requiring that they reproduce the correct exchange-correlation energy and exchange-correlation potential (up to a constant). For comparison, the results with the uniform electron gas local density approximation and a generalized gradient approximation are also shown.

Keywords: Exchange-correlation functionals; Spherical densities; Local density approximation

1. Introduction

The purpose of the present paper is to invert Gáspár's approach [1]: instead of obtaining the potential from the energy expression, we will use the potential to obtain the energy expression. While in Gáspár's approach, generalized by the Hohenberg–Kohn–Sham [2,3] theory, one assumes the existence of a good approximation for the exchange-correlation energy, and generates from a variational treatment a potential, this paper will follow the opposite way: Using the information given by a local potential we construct a local approximation for the exchange-correlation energy. The motivation for such an approach is the analysis of approximate functionals. Our functionals will be, by construction, 'exact' for a given system, in the sense that the variational principle yields the correct exchange-correlation potential and thus the correct density. For this density, the energy obtained will also be the exact one. Of course, as the local form yields only an approximation to the exact functionals, the functionals are not transferable. They can be used, however, for comparisons with different approximate functionals, generated using other criteria.

2. Method

The only approximation in density functional calculations is the exchange-correlation energy functional, often written as:

$$E_{\mathrm{xc}}[n] = \int \mathrm{d}^3 r\, e_{\mathrm{xc}}[n](r) \tag{1}$$

In the local density approximation (LDA) $e_{\mathrm{xc}}[n](r)$ becomes $e_{\mathrm{xc}}(n(r))$, usually obtained from uniform electron gas calculations. In order to assess the quality of approximate functionals, exact values of $e_{\mathrm{xc}}[n](r)$ are desirable. Unfortunately, there is no unique definition of $e_{\mathrm{xc}}[n](r)$. For example, any function f_0 which satisfies $\int \mathrm{d}^3 r f_0 = 0$ can be added to $e_{\mathrm{xc}}[n](r)$ to yield the same E_{xc}. Thus, supplementary requisites are needed in order to fix $e_{\mathrm{xc}}[n](r)$. Examples can be

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[☆] Dedicated to Professor R. Gáspár on the occasion of his 80th year.

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found, e.g. in Refs. [4–7]. In the present paper we will study spherically symmetric monotonically decaying densities, and define a local approximation for each of them. This approach has some similitude with that of Gill and Pople [4] who consider a specific gradient approximation and that of Tozer [8], who considers hydrogenic densities.

Our argument goes as follows: we first notice that the Kohn–Sham potential is a position dependent quantity appearing in DFT. It can be routinely determined (see e.g. Ref. [9] and references therein) and when the external potential is known, the exchange-correlation potential is immediately determined. The exchange-correlation potential is also the functional derivative of E_{xc} with respect to n:

$$v_{xc}(r) = \frac{\partial E_{xc}}{\partial n(r)}. \tag{2}$$

We will now *assume* that for a given system we can write E_{xc} in a local form:

$$E_{xc}^{local}[n] = \int d^3r\, e_{xc}(n(r))$$

which yields

$$v_{xc}^{local}(r) = \frac{de_{xc}}{dn}. \tag{3}$$

We require that $v_{xc}^{local}(r)$ equals the exact exchange-correlation potential $v_{xc}(r)$. Consider now:

$$\nabla e_{xc} = \frac{de_{xc}}{dn}\nabla n = v_{xc}(r)\nabla n. \tag{4}$$

To integrate this equation, we will consider spherically symmetric systems, where we have:

$$e_{xc}(r) - e_{xc}(r \longrightarrow \infty) = -\int_r^\infty \frac{dn(r')}{dr'} v_{xc}(r')\, dr'. \tag{5}$$

We will choose $e_{xc}(r \longrightarrow \infty) = 0$, as using a finite $e_{xc}(r \longrightarrow \infty)$ produces a divergent exchange-correlation energy via $\int_0^\infty 4\pi r^2 e_{xc}(r)\, dr$.

Notice that the Kohn–Sham potential is only determined up to a constant. Adding a constant to a given potential will not modify the density produced by it. The fact that the density determines the external potential up to a constant has been already pointed out by Hohenberg and Kohn [2] and physically significant changes have been analyzed by Perdew et al. [10]. More recently, Tozer and Handy [11] have greatly stressed the importance of adding a constant when constructing approximate density functionals.

We will now use the freedom in choosing this constant by asking that not only the exchange-correlation potential should be reproduced, but also the exchange-correlation energy. We re-write Eq. (5) as:

$$e_{xc}(r) = -\int_r^\infty \frac{dn(r')}{dr'}(v_{xc}^0(r') + C)\, dr' \tag{6}$$

where $v_{xc}^0(r)$ is the potential which goes to 0 as $r \longrightarrow \infty$, and require that:

$$\begin{aligned} E_{xc}^{local}[n] &= \int_0^\infty 4\pi r^2 e_{xc}(r)\, dr \\ &= -\int 4\pi r^2\, dr \int_r^\infty \frac{dn(r')}{dr'}(v_{xc}^0(r') + C)\, dr' \\ &= -\frac{4\pi}{3}\int_0^\infty \frac{dn(r)}{dr} v_{xc}^0(r) r^3\, dr + CN \end{aligned} \tag{7}$$

equals the exact exchange-correlation energy, $E_{xc}[n]$. The last equality has been obtained by changing the order of integration, and $N = \int n(r) d^3r$ is the number of electrons in the system. We will now restrict our density to be monotonically decaying. By this one-to-one correspondence between r and n we can obtain $\epsilon_{xc}(n) = e_{xc}(n(r))$.

3. Results

As a first example let us consider the hydrogenic atom ($N = 1$). The exchange-correlation energy has to exactly cancel the Hartree energy in this case:

$$E_{xc}[n] = -\frac{1}{2}\int\int \frac{n(r)n(r')}{|r - r'|} d^3r\, d^3r' \tag{8}$$

and the exchange-correlation potential is:

$$v_{xc}^0(r) = -\int \frac{n(r')}{|r - r'|} d^3r'. \tag{9}$$

By substituting $n(r)$ by

$$n_\zeta = \frac{\zeta^3}{\pi} e^{-2\zeta r}$$

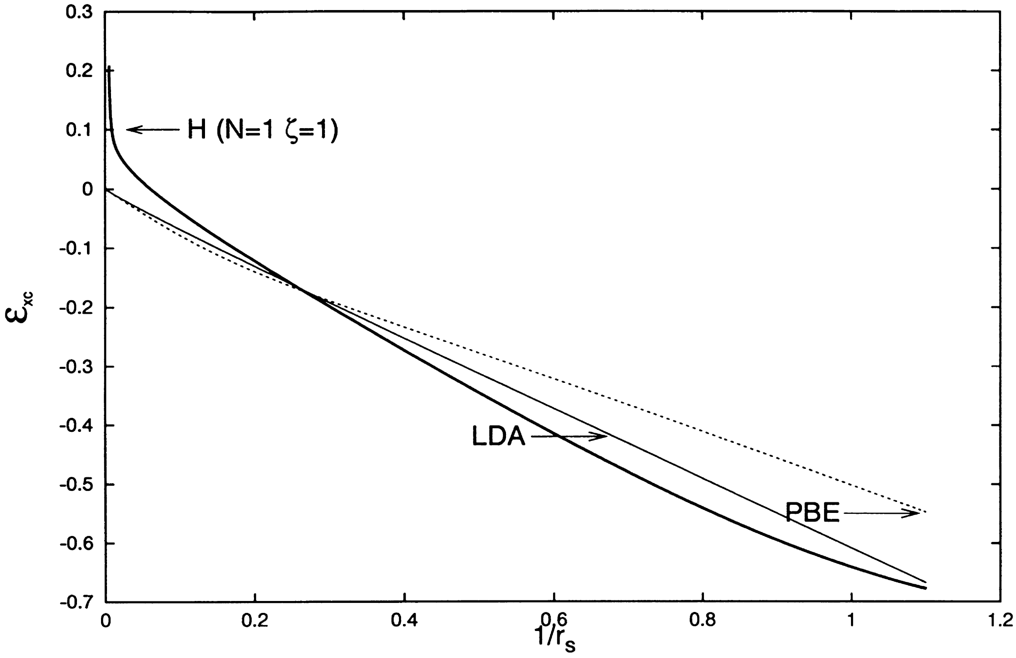

Fig. 1. Local exchange-correlation energy functional $\epsilon_{xc} = e_{xc}/n$, (Eq. (16)) as a function of $1/r_s = (4\pi n/3)^{1/3}$ for the hydrogen atom. For comparison the uniform electron gas (LDA) exchange-correlation energy density is shown as the nearly straight line and the generalized gradient approximation (PBE) exchange-correlation energy density as a dotted curve.

into the last expression we obtain:

$$E_{xc}[n] = -\frac{5}{16}\zeta \tag{10}$$

$$v^0_{xc}(n_\zeta; r) = -\frac{1}{r}[1 - (1 + r\zeta)e^{-2\zeta r}]. \tag{11}$$

To fix the constant we use Eq. (7)

$$-\frac{5}{16}\zeta = -\frac{4\pi}{3}\int_0^\infty \frac{dn(r)}{dr} v^0_{xc}(n_\zeta; r) r^3 \, dr + C \tag{12}$$

which yields $C = 5/24\zeta$. The potential is thus the same as the one of Tozer (Eq. (8) of Ref. [8]). Thus, with $v_{xc} = v^0_{xc} + C$:

$$e_{xc}(r) = -\int_r^\infty \frac{dn(r')}{dr'} v_{xc}(n_{N,\zeta}; r') dr' \tag{13}$$

$$= \frac{\zeta^4}{\pi}\left[\frac{1}{2}e^{-4\zeta r} + \frac{5}{24}e^{-2\zeta r} - 2E_1(2\zeta r) + 2E_1(4\zeta r)\right] \tag{14}$$

where $E_1(z) = \int_z^\infty t^{-1}e^{-t}\, dt$ is the exponential integral. As $2\zeta r = -\ln(\pi n/\zeta^3)$ we can obtain $e_{xc}(n)$ for $n \in (0, \zeta^3/\pi]$:

$$e_{xc}(n) = \frac{5\zeta}{24}n + \frac{\pi}{2\zeta^2}n^2 + \frac{2\zeta^4}{\pi}\left[E_1\left(-2\ln\left(\frac{\pi n}{\zeta^3}\right)\right) - E_1\left(-\ln\left(\frac{\pi n}{\zeta^3}\right)\right)\right]. \tag{15}$$

Commonly $\epsilon_{xc}(n) = e_{xc}(n)/n$ is used:

$$\epsilon_{xc}(n) = \frac{5\zeta}{24} + \frac{\pi}{2\zeta^2}n + \frac{2\zeta^4}{\pi n}\left[E_1\left(-2\ln\left(\frac{\pi n}{\zeta^3}\right)\right) - E_1\left(-\ln\left(\frac{\pi n}{\zeta^3}\right)\right)\right] \tag{16}$$

In the uniform electron gas ϵ_{xc} is proportional to $1/r_s = (4\pi n/3)^{1/3}$. We thus show, in Fig. 1, $\epsilon_{xc}(n)$ as a function of $1/r_s$. One surprising feature is the positive ϵ_{xc} for small densities (or small $1/r_s$) :

$$\lim_{n\to 0} \epsilon_{xc}(n) = \frac{5}{24}\zeta + \cdots. \tag{17}$$

The value for this limit is exactly the shift we made in the potential. The positive exchange-correlation density in the region of low density is not numerically relevant for obtaining E_{xc}, as ϵ_{xc} is weighted by the density when computing the integral. Comparing our 'exact' ϵ_{xc} with the one obtained in LDA one notices that except their behavior at small densities, the transfer from the uniform electron gas behaves quite well, in spite of the fact that E_{xc} has only to correct for the self-interaction.

The following examples have been obtained numerically. The necessary Kohn–Sham potentials and densities are taken from Ref. [12] and web-site [13]. The systems considered are: the exponential densities $n_{N,\zeta}(r) = N(\zeta^3/\pi)\, e^{-2\zeta r}$ with $N = 2$ and $\zeta = 1$, $\zeta = 2$; the He atom; the Ne^{8+} ion; the Be atom; the Ne^{6+} ion. For comparison, results obtained within the LDA and a generalized gradient approximation (PBE) [14] are also shown.

For the atomic systems, small irregularities may appear in the region of large $1/r_s (r \to 0)$, due to the use of Gaussian type orbitals (see Ref. [12]).

The exponential density $n_{N=2;\, \zeta=1}$ corresponds to that given by doubly occupied hydrogen 1s orbital (cf. Fig. 2). It yields $\epsilon_{xc}(n)$ with a general similar behavior to that observed for H.

By doubly occupying the He^+ 1s orbital ($N = 2$; $\zeta = 2$), one obtains a similar curve for ϵ_{xc} as for $\zeta = 1$: there is a significant domain where the 'exact' and approximate curves are close (cf. Figs. 2 and 3).

It is certainly no surprise that curves for He and Ne^{8+} show a similar behavior as those for the exponential densities with $N = 2$ (cf. Figs. 2, 4 and 5). The behavior for Be and the isoelectronic Ne^{6+} ($N = 4$, Figs. 6 and 7) show, however a jump around the 1s–2s shell frontier (more pronounced for Ne^{6+}). The uniform electron gas or PBE have a similar slope, but are not able to follow the jump. Interestingly, the gradient correction detects the jump, but is not strong enough.

Due to the recent interest in the value of $v_{xc}(r \to \infty)$, [11,10] we show in Table 1 together with our constants C, the values of $(I - A)/2$ (I: the ionization energy, A: the electron affinity), which is the jump in the exact v_{xc} for an infinitesimal increase in N [10].

One might think that the type of approximation proposed could give also a reasonable approximation

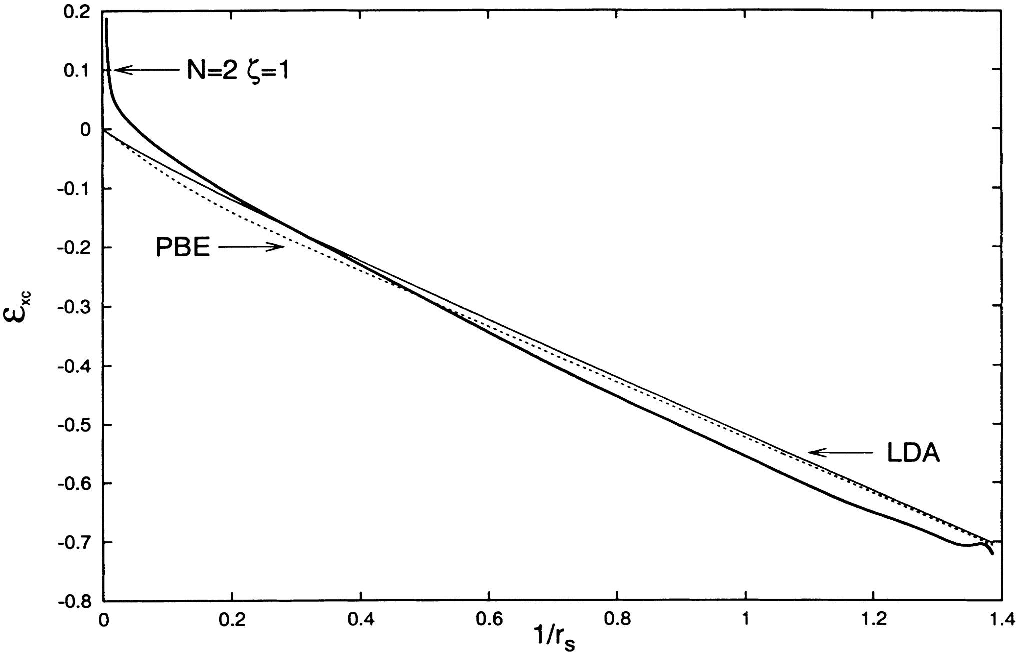

Fig. 2. Local exchange-correlation energy density ϵ_{xc}, as a function of $1/r_s$ for exponential densities $n_{N=2;\, \zeta=1}$. For comparison the uniform electron gas (LDA) exchange-correlation energy density and the generalized gradient approximation (PBE) are shown.

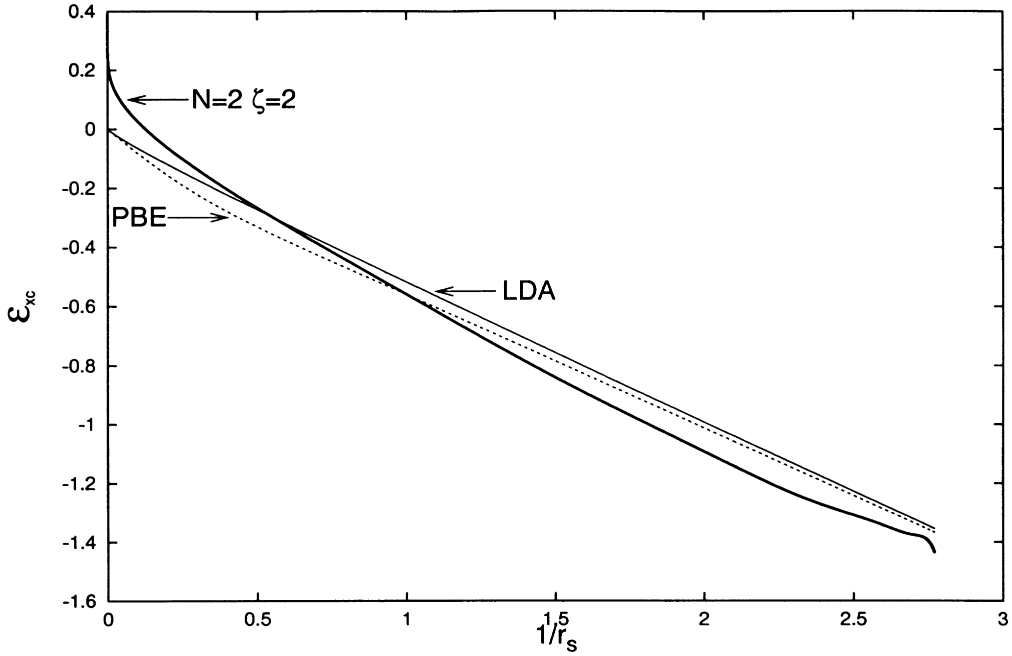

Fig. 3. Local exchange-correlation energy density ϵ_{xc}, as a function of $1/r_s$ for exponential densities $n_{N=2;\ \zeta=2}$. For comparison the uniform electron gas (LDA) exchange-correlation energy density and the generalized gradient approximation (PBE) are shown.

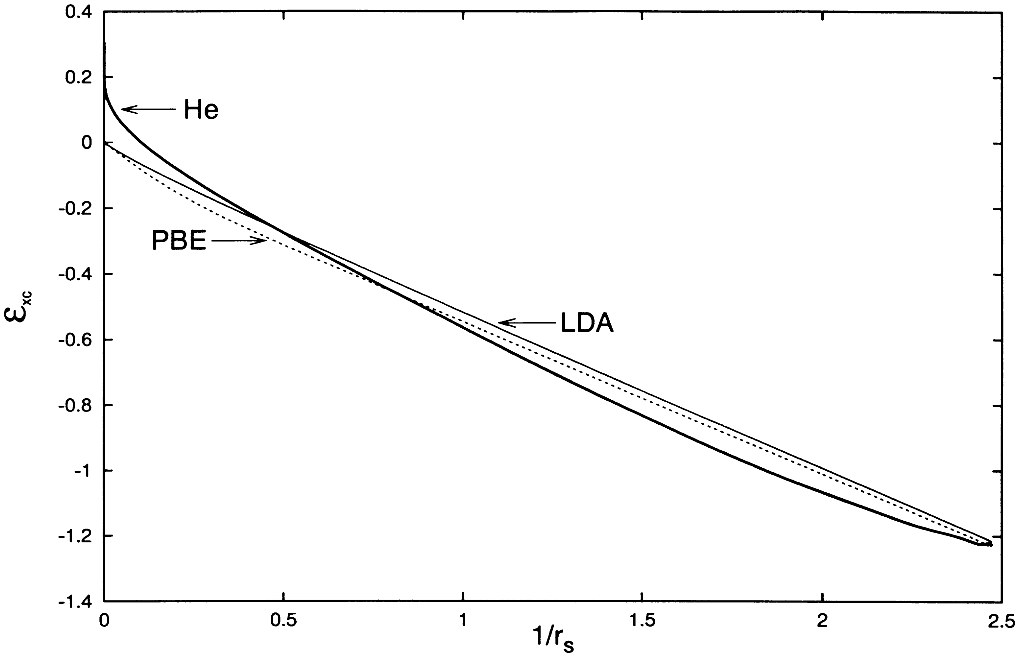

Fig. 4. Local exchange-correlation energy density ϵ_{xc}, as a function of $1/r_s$ for Helium atom. For comparison the uniform electron gas (LDA) exchange-correlation energy density and the generalized gradient approximation (PBE) are shown.

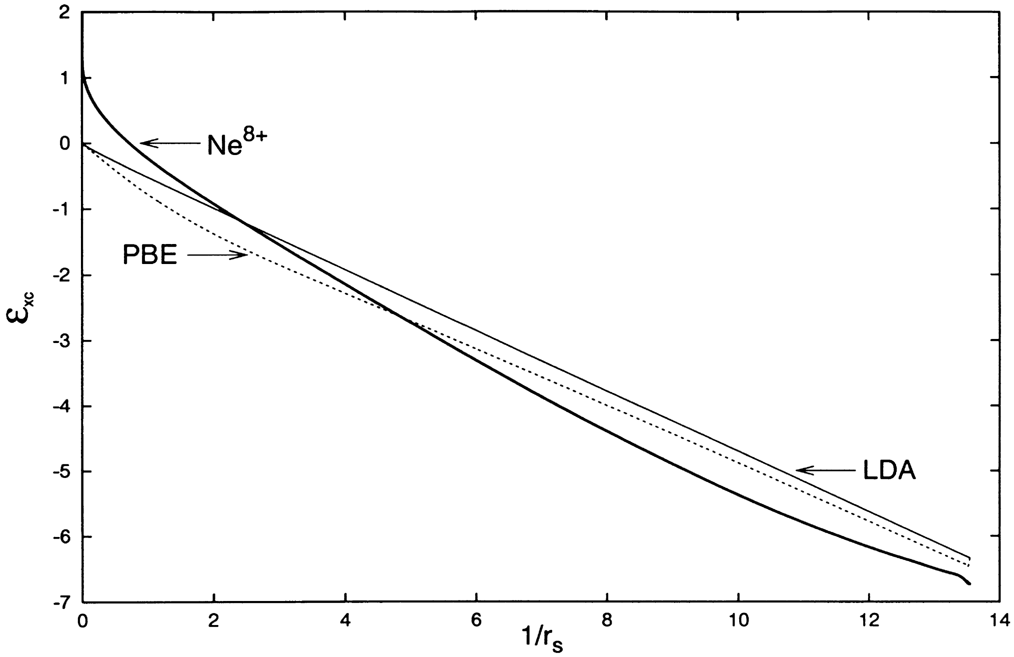

Fig. 5. Local exchange-correlation energy density ϵ_{xc}, as a function of $1/r_s$ for Ne^{8+} ion. For comparison the uniform electron gas (LDA) exchange-correlation energy density and the generalized gradient approximation (PBE) are shown.

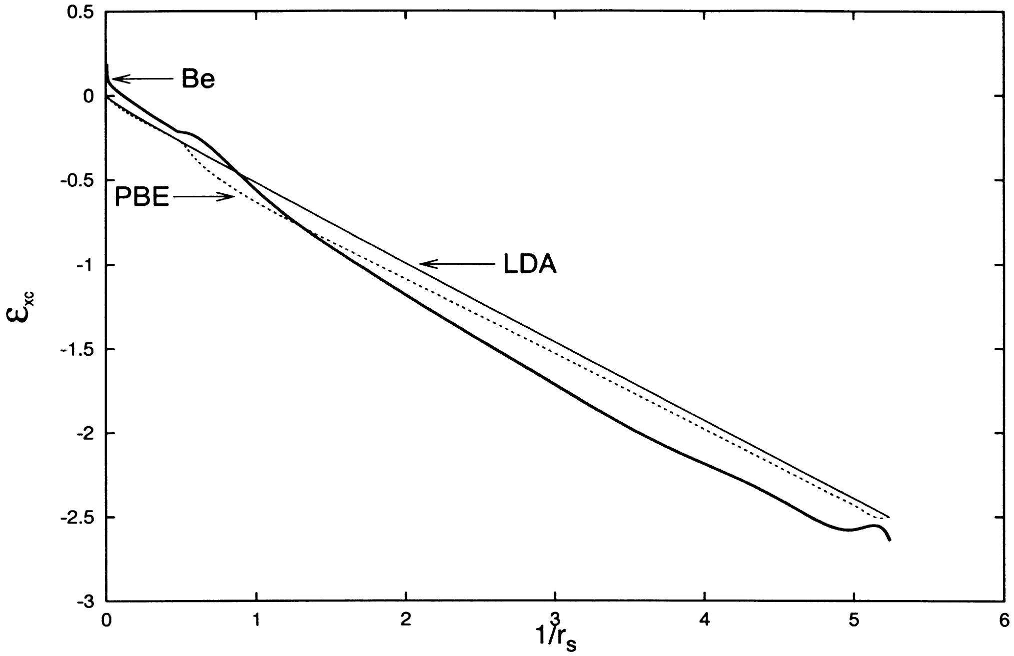

Fig. 6. Local exchange-correlation energy density ϵ_{xc}, as a function of $1/r_s$ for Beryllium atom. For comparison the uniform electron gas (LDA) exchange-correlation energy density and the generalized gradient approximation (PBE) are shown.

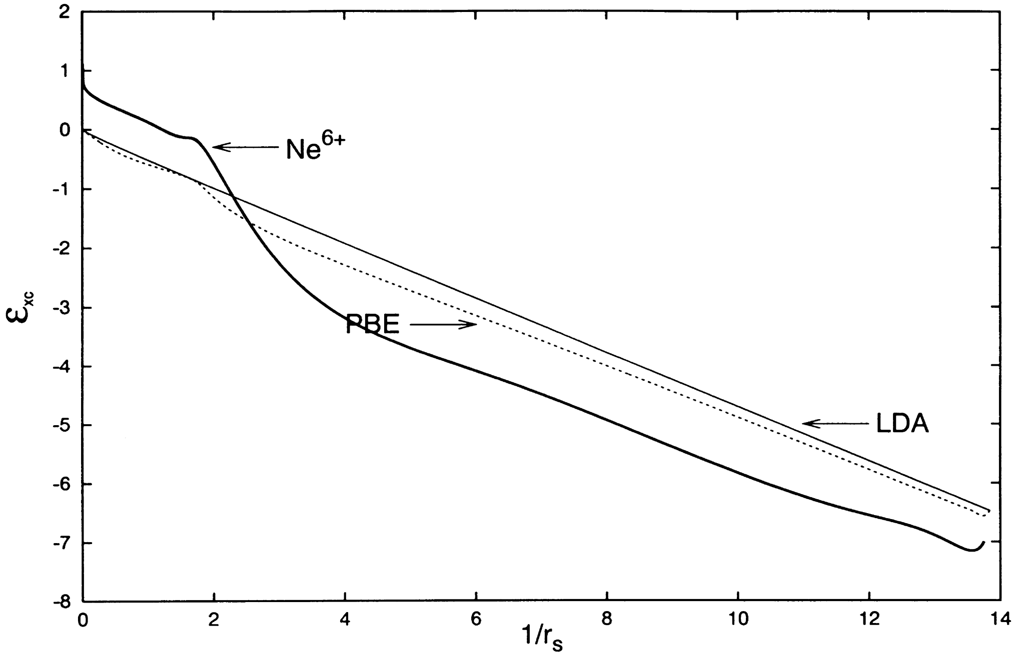

Fig. 7. Local exchange-correlation energy density ϵ_{xc}, as a function of $1/r_s$ for Ne^{6+} ion. For comparison the uniform electron gas (LDA) exchange-correlation energy density and the generalized gradient approximation (PBE) are shown.

for

$$E_h = \frac{1}{2}\int \frac{n(r_1)n(r_2)}{|r_1 - r_2|} d^3r_1\, d^3r_2. \tag{18}$$

Following the same steps as for hydrogen, we get the expression:

$$\epsilon_h = -\frac{5\zeta}{24} - \frac{\pi}{2\zeta^2}n - \frac{2\zeta^4}{\pi n}\left[E_1\left(-2\ln\left(\frac{\pi n}{\zeta^3}\right)\right) - E_1\left(-\ln\left(\frac{\pi n}{\zeta^3}\right)\right)\right]. \tag{19}$$

It thus turns out that ϵ_h is clearly more sensitive to N than to ζ (cf. Fig. 8). LDA was working reasonably well, however both for $n_{N=1;\zeta=1}$ and $n_{N=2;\zeta=1}$ (cf. Figs. 1 and 2). Thus, it seems easier to produce approximate functionals for E_{xc} than for E_h.

4. Conclusions

We have constructed local approximations to the exchange-correlation functional for H, He, Ne^{8+}, Be, Ne^{6+} as well as for exponential densities. For each of these systems, they are exact in the sense that:

- they give, via Eq. (7), the exact exchange-correlation energy,
- their functional derivatives give (up to a constant) the exact exchange-correlation potential (cf. Eq. (6)); thus the exact density can be produced via the Kohn–Sham equations.

These functionals are not transferable from one system to another, but can be compared among themselves and with common approximations.

Table 1
Asymptotic value of the exchange-correlation potential, C from Eq. (7), and difference between the ionization energy, I, and the electron affinity, A (taken from Ref. [15] and web-site [16])

System	C	$(I - A)/2$
H	0.2083	0.2353
He^+	0.4167	0.5501
He	0.3049	0.4498
Be	0.1891	0.1713

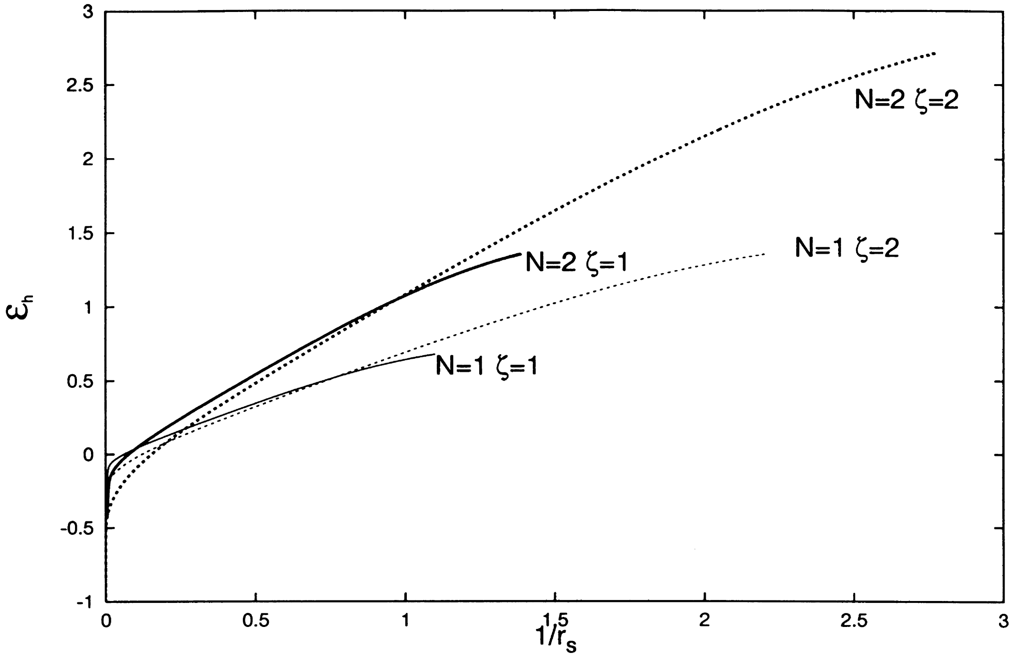

Fig. 8. Local Hartree energy density ϵ_h, as a function of $1/r_s$ for four exponential densities $n_{N;\zeta}$, for $N = 1$, $N = 2$ and $\zeta = 1$, $\zeta = 2$.

Both the uniform electron gas and the PBE reproduce grossly the trends of the one- and two-electron systems. For Be and Ne^{6+}, however, there is a jump in our functional which seems hard to recover by the common functionals.

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