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Generalized gradient approximations to density functional theory: comparison with exact results

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In order to assess the accuracy of commonly used approximate exchange-correlation density functionals, we present a comparison of accurate exchange and correlation potentials, exchange energy densities and energy components with the corresponding approximate quantities. Four systems are used as illustrative examples: the model system of two electrons in a harmonic potential and the He, Be and Ne atoms. A new ingredient in the paper is the separation of the exchange-correlation potential into exchange and correlation according to the density functional theory definition.

1. INTRODUCTION

Within density functional theory (DFT), the ground state energy of an interacting system of electrons in an external potential can be written as a functional of the ground state electronic density [1]. When compared to conventional quantum chemistry methods, this approach is particularly appealing since it does not rely on the knowledge of the complete N-electron wave function but only of the electronic density. Unfortunately, although the theory is in principle exact, the energy functional contains an unknown quantity, called the exchange-correlation energy, $E_{\rm xc}[\rho]$, that must be approximated in any practical implementation of the method. Several approximate exchange-correlation functionals have been proposed in the literature, the most commonly used ones being the local density approximation (LDA) and the generalized gradient approximation (GGA).

The local density approximation [2] is the simplest and most widely used exchange-correlation functional:

$$E_{\rm xc}^{\rm LDA}[\rho] = \int \rho(\mathbf{r})\, \epsilon_{\rm xc}^{\rm LDA}(\rho(\mathbf{r}))\, {\rm d}\mathbf{r}, \qquad (1)$$

where $\epsilon_{\rm xc}^{\rm LDA}(\rho)$ is the exchange-correlation energy per particle of a homogeneous electron gas of density ρ. $E_{\rm xc}^{\rm LDA}[\rho]$ is by definition the exact functional for a homogeneous electron gas and has been shown to give also a qualitatively good description of the ground state properties of a variety of highly inhomogeneous systems [3]. However, LDA does not always provide sufficiently accurate results. For example, it almost always overestimates the binding energy and underestimates the bond-length of weakly bound molecules and solids [3]. LDA fails also to predict the ground state structure of iron, although the error is quantitatively small [4].

In an attempt to improve upon LDA, a dependence of the exchange-correlation energy on the derivatives of the electronic density can be introduced. A simple and systematic extension of LDA is the gradient expansion approximation (GEA) [2],

$$E_{\mathrm{xc}}^{\mathrm{GEA}}[\rho] = \int \rho(\mathbf{r})\epsilon_{\mathrm{xc}}^{\mathrm{LDA}}(\rho(\mathbf{r}))\,\mathrm{d}\mathbf{r} + \int B_{\mathrm{xc}}(\rho(\mathbf{r}))|\nabla\rho(\mathbf{r})|^2\,\mathrm{d}\mathbf{r} + \cdots, \tag{2}$$

which is is asymptotically valid for densities that vary slowly over space. For finite systems, the terms in the expansion of the exchange energy of order greater or equal than four diverge while the exchange potential diverges already at second order. By using a constant B_{xc} determined variationally for each atom, Herman *et al.* showed that the gradient expansion up to second order yields improved total energies of atoms [5]. An improvement in the exchange energies is also obtained when the exact expansion coefficient for exchange, B_{x}, is used in an exchange-only calculation [6]. However, the inclusion of correlation in the second order expansion gives energies that are less accurate than LDA [7,8].

The analysis of this failure has lead some authors [9,10] to introduce a generalization of the gradient expansion, whose generic functional form (here restricted to second-order derivative) is

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[\rho] = \int \rho(\mathbf{r})\,\epsilon_{\mathrm{xc}}^{\mathrm{GGA}}(\rho(\mathbf{r}), |\nabla\rho(\mathbf{r})|\,, \nabla^2\rho(\mathbf{r}))\,\mathrm{d}\mathbf{r}. \tag{3}$$

Many different GGA's have been proposed since then [9,11–18] but none of them is clearly better than the others. Other classes of approximate functionals have also been tested, including schemes that remove the self-interaction of electrons [19,20], the weighted density approximation [21,22] and the average density approximation [21] that attempt to model the exchange-correlation hole. However, generalized gradient approximations have recently received particular attention both in the physics and chemistry communities since they do not add appreciable computational complexity to the LDA scheme.

The GGA functionals seem to give a good description of several finite systems: they significantly improve total energies of atoms [23], as well as binding energies [23–26] and vibrational frequencies [24] of first and second-row molecules. They also give better estimates of bond-lengths and binding energies of weakly bound systems such as IIA and IIB homonuclear dimers [27] and hydrogen bonded systems [28], which are greatly overbound in LDA. Lattice constants, bulk moduli and cohesive energies of simple metals [23] and $3d$ transition metals [29] are also improved. For iron, the correct ferromagnetic bcc ground state is predicted [29]. On the other hand, the lattice constants and the bulk moduli of the semiconductors Si, Ge and GaAs are less accurately predicted by the GGA's than LDA, the effect being particularly large for the bulk moduli [30]. Calculations for $4d$ and $5d$ metals indicate that, while LDA tends to slightly underestimate lattice constants and overestimate bulk moduli, GGA's often overcorrect, sometimes leading to results in worse agreement with experiment [31]. The tendency of the GGA's to yield smaller binding energies and larger bond-lengths than LDA is explained by the fact that the GGA's favor inhomogeneity in the density. Since isolated atoms are more inhomogeneous than molecules or solids, the energy of the atoms is lowered more, resulting in smaller binding energies. Similarly, for weakly bound systems, larger bond-lengths lead to increased inhomogeneity and are therefore favored by the GGA's.

Studies that compare the predicted structural and energetic properties of various systems with the corresponding experimental quantities add very little to the understanding of the reasons for the successes or the failures of the approximate functionals. In order to gain more insight into the limitations of the approximate functionals, many researchers [32–47] have compared accurate density functional properties, calculated by more sophisticated and more computationally demanding methods, with the corresponding density functional properties calculated from the approximate functionals. In this review, we limit ourselves to some of our earlier work and discuss four systems, for which it is possible to obtain exact or very accurate wave functions, as illustrative examples: a model system of two electrons in a harmonic potential and the He, Be and Ne atoms. While, we mostly concentrate on the description of our previous work, there is a new ingredient in this paper: the separation of the exchange-correlation potential of many-electron systems into separate exchange and correlation components according to the DFT definition.

The outline of the rest of the paper is as follows. In Sec. 2, we briefly introduce density functional theory and its Kohn-Sham formulation. In Sec. 3, we list some properties of the exact exchange-correlation functional and we determine which properties are satisfied or violated by LDA and various GGA's. The short and long distance asymptotic behavior of the exchange-correlation potential and local exchange energy per electron is also discussed. In Sec. 4, we derive the formulae used to determine the exact density functional quantities and, in Sec. 5, we describe the systems we study and the corresponding densities. The exact exchange and correlation potentials, local exchange energies per electron and components of the total energy of these systems are compared with the corresponding approximate LDA and GGA quantities in Secs. 6, 7 and 8, respectively. In Sec. 9, we summarize our conclusions and discuss some prospects for better approximate functionals. In Appendix A, we list the approximate functionals used in the comparison.

2. THEORETICAL BACKGROUND

Density functional theory provides an expression for the ground state energy of a system of interacting electrons in an external potential as a functional of the ground state electronic density [1]. Let us assume for simplicity that the spin polarization of the system of interest is identically zero. In the Kohn-Sham formulation of density functional theory [2], the ground state density is written in terms of single-particle orbitals obeying the equations in atomic units ($\hbar = e = m = 1$):

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' + v_{\rm xc}\left([\rho]\,;\mathbf{r}\right)\right\}\psi_i = \epsilon_i\psi_i, \tag{4}$$

where

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 . \tag{5}$$

The electronic density is constructed by summing over the N lowest energy orbitals where N is the number of electrons. $v_{\mathrm{ext}}(\mathbf{r})$ is the external potential. The exchange-correlation potential $v_{\mathrm{xc}}([\rho]\,;\mathbf{r})$ is the functional derivative of the exchange-correlation energy $E_{\mathrm{xc}}[\rho]$ that enters in the expression for the total energy of the system:

$$E = -\frac{1}{2}\sum_{i=1}^{N}\int \psi_i \nabla^2 \psi_i \,\mathrm{d}\mathbf{r} + \int \rho(\mathbf{r})\, v_{\mathrm{ext}}(\mathbf{r})\,\mathrm{d}\mathbf{r} + \frac{1}{2}\int\!\!\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' + E_{\mathrm{xc}}[\rho] . \tag{6}$$

The exchange-correlation functional is written as the sum of two separate contributions for exchange and correlation,

$$E_{\mathrm{xc}}[\rho] = E_{\mathrm{x}}[\rho] + E_{\mathrm{c}}[\rho] . \tag{7}$$

The definition of the exchange energy is in terms of the non-interacting wave function Φ_0, the Slater determinant constructed from the Kohn-Sham orbitals, as

$$E_{\mathrm{x}}[\rho] = \langle \Phi_0 |\, V_{\mathrm{ee}} \,| \Phi_0 \rangle - \frac{1}{2}\int\!\!\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}', \tag{8}$$

where V_{ee} is the electron-electron interaction. This definition differs from the conventional quantum chemistry definition of E_{x} as the exchange energy in a Hartree-Fock calculation, given by the same expression as in Eq. 8 but with the Kohn-Sham determinant replaced by the Hartree-Fock determinant. The separation of the exchange-correlation energy functional into the separate exchange and correlation components yields a corresponding splitting of the exchange-correlation potential into $v_{\mathrm{x}}([\rho]\,;\mathbf{r})$ and $v_{\mathrm{c}}([\rho]\,;\mathbf{r})$. In this formulation, the essential unknown quantity is the exchange-correlation energy $E_{\mathrm{xc}}[\rho]$. If the functional form of $E_{\mathrm{xc}}[\rho]$, and consequently the exchange-correlation potential, were available, we could solve the N-electron problem by finding the solution of a set of single-particle equations. However, as mentioned in Sec. 1, the exact functional form of $E_{\mathrm{xc}}[\rho]$ is not known and it is necessary to make approximations for this term.

3. PROPERTIES OF THE EXACT DENSITY FUNCTIONAL

In order to understand if it is possible to construct an approximate functional that does not suffer from the weaknesses of the existing GGA's, it is useful to study the known properties of the exact density functional and which of these are violated by the commonly used approximate functionals. There are actually a surprisingly large number of known properties [48–53] and some of these are listed in Table 1. The GGA functionals compared in the table can be found in Appendix A.

The first group of properties in Table 1 are sum rules that are satisfied by the exchange and correlation holes. The exchange-correlation energy functionals can be interpreted as

Table 1
Some properties of the exact exchange-correlation functional. Comparison with approximate functionals. Taken from Ref. [45] and modified.

	Property	$E_{\mathrm{xc}}^{\mathrm{LDA}}$ [15]	$E_{\mathrm{xc}}^{\mathrm{LM}}$ [9]	$E_{\mathrm{xc}}^{\mathrm{PW91}}$ [14]	$E_{\mathrm{x}}^{\mathrm{B88}}$ [11]	$E_{\mathrm{x}}^{\mathrm{ECMV}}$ [18]	$E_{\mathrm{c}}^{\mathrm{WL}}$ [16]	$E_{\mathrm{c}}^{\mathrm{LYP}}$ [17]
1	$\rho_{\mathrm{x}}(\mathbf{r},\mathbf{r}') \leq 0$	Y	—	Y	—	—	—	—
2	$\int \rho_{\mathrm{x}}(\mathbf{r},\mathbf{r}')\,\mathrm{d}\mathbf{r}' = -1$	Y	—	Y	—	—	—	—
3	$\int \rho_{\mathrm{c}}(\mathbf{r},\mathbf{r}')\,\mathrm{d}\mathbf{r}' = 0$	Y	—	Y	—	—	—	—
4	$E_{\mathrm{x}}[\rho] < 0$	Y	Y	Y	Y	Y	—	—
5	$E_{\mathrm{c}}[\rho] \leq 0$	Y	N	N	—	—	N	N
6	$E_{\mathrm{x}}[\rho], E_{\mathrm{xc}}[\rho] \geq -c\int \rho^{4/3}\,\mathrm{d}\mathbf{r}$ [a]	Y	N	Y	N	N	—	—
7	$E_{\mathrm{x}}[\rho_\lambda] = \lambda E_{\mathrm{x}}[\rho]$	Y	Y	Y	Y	Y	—	—
8	$E_{\mathrm{c}}[\rho_\lambda] < \lambda E_{\mathrm{c}}[\rho],\ \lambda < 1$ [b]	Y	N	Y	—	—	N	N
9	$\lim_{\lambda\to\infty} E_{\mathrm{c}}[\rho_\lambda] > -\infty$	N	Y [c]	Y [c]	—	—	Y	Y
10	$\lim_{\lambda\to 0} \frac{1}{\lambda} E_{\mathrm{c}}[\rho_\lambda] > -\infty$	Y	N	Y	—	—	Y	Y
11	$\lim_{\lambda\to\infty} E_{\mathrm{x}}[\rho_\lambda^{\mathrm{x}}] > -\infty$	N	N	Y	N	N	—	—
12	$\lim_{\lambda\to 0} E_{\mathrm{x}}[\rho_\lambda^{\mathrm{x}}] > -\infty$	Y	N	Y	Y	Y	—	—
13	$\lim_{\lambda\to\infty} \frac{1}{\lambda} E_{\mathrm{x}}[\rho_\lambda^{\mathrm{xy}}] > -\infty$	Y	N	Y	Y	Y	—	—
14	$\lim_{\lambda\to 0} \frac{1}{\lambda} E_{\mathrm{x}}[\rho_{\lambda\lambda}^{\mathrm{xy}}] > -\infty$	N	N	Y	N	N	—	—
15	$\lim_{\lambda\to\infty} \lambda E_{\mathrm{c}}[\rho_\lambda^{\mathrm{x}}] > -\infty$	N	Y [c]	Y	—	—	N	N
16	$\lim_{\lambda\to 0} \frac{1}{\lambda} E_{\mathrm{c}}[\rho_\lambda^{\mathrm{x}}] = 0$	N	N	Y	—	—	N	N
17	$\lim_{\lambda\to\infty} E_{\mathrm{c}}[\rho_{\lambda\lambda}^{\mathrm{xy}}] = 0$	N	N	Y	—	—	N	N
18	$\lim_{\lambda\to 0} \frac{1}{\lambda^2} E_{\mathrm{c}}[\rho_{\lambda\lambda}^{\mathrm{xy}}] > -\infty$	N	Y [c]	Y	—	—	Y [c]	N
19	$\epsilon_{\mathrm{x}}(r) \to -1/2r,\quad r\to\infty$	N	N	N	YN [d]	N	—	—
20	$v_{\mathrm{x}}(r) \to -1/r,\quad r\to\infty$	N	N	N	N	N	—	—
21	$v_{\mathrm{x}}(r), v_{\mathrm{c}}(r)$ finite, $r\to 0$	Y	N	N	N	N	N	N
22	LDA limit for constant ρ	Y	N	Y	Y	Y	N	N
23	GEA limit for slowly varying ρ	—	N	Y	N	N	N	N

[a] $1.44 < c < 1.68$

[b] Note that $E_{\mathrm{c}}[\rho_\lambda] < \lambda E_{\mathrm{c}}[\rho],\ \lambda < 1$ is equivalent to $E_{\mathrm{c}}[\rho_\lambda] > \lambda E_{\mathrm{c}}[\rho],\ \lambda > 1$.

[c] But it diverges to $+\infty$. The PW91 GGA can be modified to satisfy this relation [49].

[d] "Y" for exponential $\rho(\mathbf{r})$ but "N" in general, *e.g.* $\epsilon_{\mathrm{x}}^{\mathrm{B88}}(r) \to -1/r$ for a Gaussian density.

the energy arising form the interaction of an electron at $\mathbf{r}$ and its exchange-correlation hole at $\mathbf{r}'$,

$$E_{\mathrm{xc}}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\,\rho_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'. \tag{9}$$

The exchange-correlation hole is then separated into exchange and correlation, $\rho_{\mathrm{x}}(\mathbf{r},\mathbf{r}')$ and $\rho_{\mathrm{c}}(\mathbf{r},\mathbf{r}')$ respectively, where the exchange contribution comes from the non-interacting system according to Eq. 8. The exchange-correlation hole can be expressed as an integral over the coupling constant of the density-density correlation function of the interacting system [48].

The second group of properties provide bounds on the functionals. Condition 6 is known as the Lieb-Oxford bound and a tighter version of it is given in Ref. [49]:

$$\lim_{\lambda\to 0} \frac{1}{\lambda} E_{\mathrm{xc}}[\rho_\lambda] = \inf_{\Psi\to\rho} \langle \Psi | V_{\mathrm{ee}} | \Psi \rangle - \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \geq -c \int \rho(\mathbf{r})^{4/3}\,\mathrm{d}\mathbf{r}, \tag{10}$$

where the density ρ_λ is obtained by uniformly scaling the density ρ in all three spatial directions:

$$\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda\mathbf{r}). \tag{11}$$

This scaled density integrates to the same number of electrons as the unscaled one.

The scaling of the exchange and correlation functionals when the charge density is scaled uniformly [50,51] is described by the third group of properties. It now becomes evident why it is useful to separate the exchange component from the entire functional according to Eq. 8. For exchange, an exact relation (condition 7) exists under uniform density scaling that determines how derivatives of the density combine with the density in an exchange GGA functional:

$$E_{\mathrm{x}}^{\mathrm{GGA}}[\rho] = \int \rho(\mathbf{r})^{4/3}\, F(\,|\nabla\rho(\mathbf{r})|\,/\rho(\mathbf{r})^{4/3}, \nabla^2\rho(\mathbf{r})/\rho(\mathbf{r})^{5/3}, \ldots)\,\mathrm{d}\mathbf{r}. \tag{12}$$

The fourth set of properties consists of the relations under non-uniform scaling of the density in one or two of the spatial directions:

$$\rho_\lambda^{\mathrm{x}}(\mathbf{r}) = \lambda\,\rho(\lambda x, y, z), \quad \rho_{\lambda\lambda}^{\mathrm{xy}}(\mathbf{r}) = \lambda^2\,\rho(\lambda x, \lambda y, z). \tag{13}$$

The non-uniform scaling relations for the correlation energy are here given in the tightest form and are derived under the assumption of the existence of a Taylor series in λ or $1/\lambda$ [52]. A summary of the scaling relations and their derivation is provided in Ref. [53].

The fifth group of properties describes the long-distance asymptotic behavior (for finite systems) of the exchange potential and the local exchange energy per electron (see Sec. 3) and the short-distance behavior of the exchange and correlation potential.

The last two conditions are that the functionals must reduce to the LDA functional in the limit of a homogeneous density and to the correct second-order expansion for a slowly varying density.

We also mention an additional relation not included in the table, the convexity constraint [49], which is given by

$$\left.\frac{\partial^2 B\left[\rho+\epsilon\Delta\rho\right]}{\partial\epsilon^2}\right|_{\epsilon=0}+\iint\frac{\Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\geq 0, \tag{14}$$

for arbitrary $\Delta\rho$ integrating to zero, where

$$B\left[\rho\right]=\lim_{\lambda\to 0}\frac{1}{\lambda}E_{\mathrm{xc}}\left[\rho_\lambda\right]. \tag{15}$$

This constraint is very stringent: it is violated by the LDA, by the Perdew-Wang '91 GGA and, likely, by any other GGA functional [49].

From Table 1, it appears that most of the functionals violate the asymptotic behavior of the exchange-correlation potential and local exchange energy per electron. Within GGA, the exchange-correlation potential is given by the functional derivative of $E_{\mathrm{xc}}^{\mathrm{GGA}}\left[\rho\right]$ (Eq. 3):

$$v_{\mathrm{xc}}\left(\left[\rho\right];\mathbf{r}\right)=\left[\frac{\partial\, e_{\mathrm{xc}}}{\partial\,\rho}-\nabla\cdot\left(\frac{\partial\, e_{\mathrm{xc}}}{\partial\,\nabla\rho}\right)+\nabla^2\left(\frac{\partial\, e_{\mathrm{xc}}}{\partial\,\nabla^2\rho}\right)\right]_{\rho(\mathbf{r}),\nabla\rho(\mathbf{r}),\nabla^2\rho(\mathbf{r})}, \tag{16}$$

where e_{xc} is the exchange-correlation energy density, $e_{\mathrm{xc}}=\rho\,\epsilon_{\mathrm{xc}}$. As pointed out in our earlier papers [54,55], any GGA that has terms containing $\nabla\rho$ but no higher derivatives of ρ must yield an exchange-correlation potential that diverges at nuclei. If $\rho\sim\mathrm{constant}+r^s$ near the origin, then $|\nabla\rho|\sim r^{s-1}$. If the leading behavior of e_{xc} in the gradient, near an extremum of the density, is $|\nabla\rho|^m$, then

$$\frac{\partial\, e_{\mathrm{xc}}}{\partial\,\nabla\rho}\sim|\nabla\rho|^{m-1}\sim r^{(s-1)(m-1)}, \tag{17}$$

and

$$\nabla\cdot\left(\frac{\partial\, e_{\mathrm{xc}}}{\partial\,\nabla\rho}\right)\sim r^{(s-1)(m-1)-1}. \tag{18}$$

Therefore, the exchange-correlation potential diverges at the origin if

$$(s-1)(m-1)-1<0, \tag{19}$$

where s and m are positive. Thus, the exchange-correlation potential diverges at extrema of the density for all values of s if $m\leq 1$, as is the case for the Wilson-Levy potential [16], and for all values of m if $s\leq 1$. At nuclei, $s=1$ so that the exchange-correlation potential always diverges.

As far as the large distance asymptotics are concerned, any GGA that includes no higher than first derivatives of the density cannot simultaneously satisfy both the correct $-1/r$ behavior of the exchange-correlation potential and the correct $-1/2r$ behavior of the local exchange-correlation energy per electron [18].

It is however possible, as mentioned in Refs. [45,55], to include the Laplacian of the density in an appropriate way [56] and construct a GGA that has the triple advantage that it satisfies both of the long-distance asymptotic conditions and also does not suffer from a spurious divergence at the nuclei. There are an infinite number of possible variations in the functional form that preserve the desired short and long range asymptotic behaviors. We are presently searching for the most physically reasonable functional expression and for a universal set of parameter values in such a functional. In the same line of research, Jemmer and Knowles have recently published a simple expression for an exchange functional depending on the Laplacian of the density and reproducing the correct long and short distance asymptotics of the exchange-correlation potential and local exchange-correlation energy per electron [57]. However, they conclude that such a functional is not a suitable choice as a general purpose density functional. The importance of Laplacian terms has also been pointed out by Engel and Vosko [58] who show that inclusion of Laplacian terms in a fourth order Taylor expansion of the exchange-correlation functional results in improved exchange potentials for atoms and jellium spheres. However, their expression does not obey any of the above three asymptotic conditions.

4. DETERMINATION OF ACCURATE DFT QUANTITIES

For atomic systems, it is possible to determine accurate exchange-only quantities by using the solution of the optimized effective potential (OEP) method which represents the exact solution in an exchange-only DFT scheme [20]. However, these quantities are determined not for the exact density but for the OEP density which corresponds to the self-consistent solution in an exchange-only approach. The performance of exchange-only approximate functionals and the corresponding exchange potentials can therefore be routinely checked for atomic systems by using the OEP method. Approximate quantities in exchange-only GGA, evaluated either for the OEP density or the self-consistent density, can be compared with the corresponding OEP quantities.

Obtaining reliable exchange-correlation potentials and energies is instead a more difficult task. One has to generate an accurate density and then compute an exchange-correlation potential that yields the desired density as a solution of the Kohn-Sham equations (Eq. 4 and 5). In this context, researchers have used charge densities, of varying degrees of accuracy, calculated by quantum chemistry methods for atoms [32–41] and molecules [42–44], as well as Quantum Monte Carlo methods for atoms [45,47] and for a model semiconductor [46]. The subsequent inverse problem, namely the search of the corresponding exchange-correlation potential, has been performed using a variety of different techniques. For example, in the special case of the singlet ground state of a two-electron system, the exchange-correlation potential can be obtained simply from Eq. 4 while, for systems with more than two electrons, $v_{\rm xc}$ can be determined by expanding it in a complete set of basis functions and varying the expansion coefficients such that Eqs. 4 and 5 yield the accurate density[34,47]. Whatever the technique used, an accurate density is a key ingredient for the determination of the exchange-correlation potential, because small errors in the density are greatly magnified by the inversion procedures used to obtain the potential.

By knowing the exchange-correlation potential, we are able to calculate the Kohn-Sham orbitals and, if the total energy of the system can be estimated, the exchange-correlation energy is obtained by inversion of the expression for the total energy (Eq. 6):

$$E_{\mathrm{xc}}[\rho] = E - \frac{1}{2}\sum_{i=1}^{N}\int \psi_i \nabla^2 \psi_i \,\mathrm{d}\mathbf{r} - \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' - \int \rho(\mathbf{r})\, v_{\mathrm{ext}}(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{20}$$

Since the Kohn-sham orbitals are known, the exchange energy (Eq. 8) can be calculated as

$$E_{\mathrm{x}}[\rho] = -\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\delta_{m_{s_i},m_{s_j}}\iint \frac{\psi_i^*(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}', \tag{21}$$

where the δ-function is over the spin quantum numbers of the i-th and j-th spin-orbitals. The correlation energy is finally obtained as the difference of the exchange-correlation energy (Eq. 20) and the exchange energy (Eq. 21):

$$E_{\mathrm{c}}[\rho] = E_{\mathrm{xc}}[\rho] - E_{\mathrm{x}}[\rho]\,. \tag{22}$$

The functional derivative of the exchange energy (Eq. 21) with respect to the density yields the exchange potential. By knowing the exchange-correlation and the exchange potentials, we obtain the correlation potential as the difference

$$v_{\mathrm{c}}([\rho];\mathbf{r}) = v_{\mathrm{xc}}([\rho];\mathbf{r}) - v_{\mathrm{x}}([\rho];\mathbf{r})\,. \tag{23}$$

We show in Sub-sec. 4.1 that it is easy to calculate the exchange potential for a system of two electron in a singlet state. The procedure is instead much more involved for a many-electron system, as we outline in Sub-sec. 4.2.

As already introduced in Sec. 1, the exchange-correlation functional can be written as an integral over the exchange-correlation energy density, $e_{\mathrm{xc}}(\mathbf{r})$, or the local exchange-correlation energy per electron, $\epsilon_{\mathrm{xc}}(\mathbf{r})$:

$$E_{\mathrm{xc}}[\rho] = \int e_{\mathrm{xc}}(\mathbf{r})\,\mathrm{d}\mathbf{r} = \int \rho(\mathbf{r})\,\epsilon_{\mathrm{xc}}(\mathbf{r})\,\mathrm{d}\mathbf{r}. \tag{24}$$

The separation of E_{xc} into exchange and correlation (Eq. 7) corresponds to an equivalent decomposition of ϵ_{xc} into ϵ_{x} and ϵ_{c}. The definition of ϵ_{xc} and its components is however not unique since two ϵ_{xc}'s whose difference is a function f with $\int \rho(\mathbf{r})\, f(\mathbf{r})\,\mathrm{d}\mathbf{r} = 0$ yield the same exchange-correlation energy functional.

We observe that a natural definition of the local exchange energy per electron follows from Eq. 21:

$$\epsilon_{\mathrm{x}}(\mathbf{r}) = -\frac{1}{2}\frac{1}{\rho(\mathbf{r})}\sum_{i=1}^{N}\sum_{j=1}^{N}\delta_{m_{s_i},m_{s_j}}\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\int \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}'. \tag{25}$$

This definition results in an ϵ_{x} that at large distances goes as $-1/2r$ [59]. A procedure for constructing ϵ_{c} has been recently proposed using first and second order density matrices from correlated wave functions and applied to He and H_2 [60].

In the remaining sections, the accurate exchange-correlation energies and potentials, the separate exchange and correlation components and the local exchange energy per electron are used to test the accuracy of the approximate exchange-correlation energy functionals listed in Appendix A.

4.1. Two-electron systems

For two electrons of opposite spin, there is a single spatial Kohn-Sham orbital ψ and is simply related to the electronic density (Eq. 5) as

$$\psi(\mathbf{r}) = \left[\frac{\rho(\mathbf{r})}{2}\right]^{1/2}. \tag{26}$$

Knowing the exact density, the exchange-correlation potential can be obtained by inversion of the Kohn-Sham equation (Eq. 4),

$$v_{\mathrm{xc}}([\rho]\,;\mathbf{r}) = \epsilon_{\mathrm{KS}} + \frac{1}{2}\frac{\nabla^2\psi}{\psi} - v_{\mathrm{ext}}(\mathbf{r}) - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'. \tag{27}$$

The eigenvalue ϵ_{KS} is equal to minus the ionization energy if we impose that the exchange-correlation potential goes to zero at infinity. Therefore, the exchange-correlation potential is completely determined. From Eq. 21, it follows that the exchange energy is given by

$$E_{\mathrm{x}}[\rho] = -\frac{1}{4}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}', \tag{28}$$

and the functional derivative of this expression with respect to the density yields the exact exchange potential:

$$v_{\mathrm{x}}([\rho]\,;\mathbf{r}) = -\frac{1}{2}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'. \tag{29}$$

Observe that $v_{\mathrm{x}}([\rho]\,;\mathbf{r})$ simply follows from the condition that it cancels the self-interaction term in the Hartree potential.

For a system of two interacting electrons in a singlet state, Eq. 25 for the local exchange energy per electron reduces to

$$\epsilon_{\mathrm{x}}(\mathrm{r}) = -\frac{1}{4}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'. \tag{30}$$

The same expression could have also been obtained from Eq. 28.

4.2. Many-electron systems

While the separation of the exchange-correlation potential into exchange plus correlation is quite simple in the two-electron systems, this decomposition according to the DFT definition has never been obtained for many-electron systems. In previous work [34,35,38,45,41], the exchange potential was defined as the difference of the effective Kohn-Sham potential yielding the Hartree-Fock density and the sum of the Hartree and the external potentials. The correlation potential was then obtained as the difference of the exchange-correlation potential corresponding to the exact density and the above potential. Note that this separation does not correspond to the DFT definition of Eq. 23: it involves two densities, the exact and the Hartre-Fock densities, while the potential used for exchange is only approximately equal to the exchange potential corresponding to the Hartree-Fock density (although very close to it) since it is not the functional derivative with respect to the density of the exchange energy evaluated for the orbitals obtained from the effective potential yielding the Hartree-Fock density. Here, we obtain the correct separation of the exchange and correlation components, according to their DFT definition, for the exact density. The difference between the exchange potential we obtain and the approximate "exchange" potential described above is almost not detectable on the scale of the exchange potential. On the other hand, on the more expanded scale of the correlation potential, the difference is clearly visible, although the shapes are very similar.

We follow Görling and Levy [61] in showing how to separate the exchange-correlation potential into exchange and correlation. We consider a spin unpolarized system. If we assume that the density ρ is non-interacting v-representable, it can be expressed as in Eq. 5 in terms of single-particle orbitals $\{\psi_i\}$ of the Kohn-Sham potential $v_{\rm s}(\mathbf{r})$,

$$v_{\rm s}(\mathbf{r}) = v_{\rm ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}' + v_{\rm xc}([\rho];\mathbf{r}). \tag{31}$$

We evaluate the functional derivative of the exchange energy functional with respect to the Kohn-Sham potential as

$$\frac{\delta E_{\rm x}[\rho]}{\delta v_{\rm s}(\mathbf{r})} = \int \frac{\delta E_{\rm x}[\rho]}{\delta \rho(\mathbf{r}')}\frac{\delta \rho(\mathbf{r}')}{\delta v_{\rm s}(\mathbf{r})}\,\mathrm{d}\mathbf{r}' = \int v_{\rm x}([\rho];\mathbf{r}')\sum_{i=1}^{N}\left(\psi_i^*(\mathbf{r}')\frac{\delta\psi_i(\mathbf{r}')}{\delta v_{\rm s}(\mathbf{r})} + \frac{\delta\psi_i^*(\mathbf{r}')}{\delta v_{\rm s}(\mathbf{r})}\psi_i(\mathbf{r}')\right)\,\mathrm{d}\mathbf{r}'. \tag{32}$$

On the other hand, since the exchange functional can be written as a function of the orbitals (Eq. 21), we also have

$$\frac{\delta E_{\rm x}[\rho]}{\delta v_{\rm s}(\mathbf{r})} = \sum_{i=1}^{N}\int\left(\frac{\delta E_{\rm x}[\rho]}{\delta\psi_i(\mathbf{r}')}\frac{\delta\psi_i(\mathbf{r}')}{\delta v_{\rm s}(\mathbf{r})} + \frac{\delta E_{\rm x}[\rho]}{\delta\psi_i^*(\mathbf{r}')}\frac{\delta\psi_i^*(\mathbf{r}')}{\delta v_{\rm s}(\mathbf{r})}\right)\,\mathrm{d}\mathbf{r}'. \tag{33}$$

If we combine Eqs. 32 and 33, we obtain the integral equation

$$\int v_{\rm x}([\rho];\mathbf{r}')\,\mathcal{K}(\mathbf{r}',\mathbf{r})\,\mathrm{d}\mathbf{r}' = \mathcal{Q}(\mathbf{r}), \tag{34}$$

where the kernel $\mathcal{K}(\mathbf{r}',\mathbf{r})$ and the right hand side $\mathcal{Q}(\mathbf{r})$ depend on the orbital $\{\psi_i\}$ and their functional derivative with respect to the potential $v_{\rm s}(\mathbf{r})$. This integral equation is equivalent to the one solved in the OEP method with the KS orbitals replaced by the OEP orbitals [20]. The functional derivatives of the orbitals $\delta\psi_i(\mathbf{r})/\delta v_{\rm s}(\mathbf{r}')$ can be expressed in terms of the Green's function $G_i(\mathbf{r},\mathbf{r}')$ as

$$\frac{\delta\psi_i(\mathbf{r})}{\delta v_{\rm s}(\mathbf{r}')} = -G_i(\mathbf{r},\mathbf{r}')\,\psi_i(\mathbf{r}'), \tag{35}$$

where $G_i(\mathbf{r}, \mathbf{r}')$ satisfies the differential equation

$$\left(-\frac{1}{2}\nabla^2 + v_{\rm s}(\mathbf{r}) - \epsilon_i\right) G_i(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') - \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}'). \tag{36}$$

By knowing the exchange-correlation potential, the KS orbitals and eigenvalues, we can compute the Green's functions $\{G_i\}$ and, consequently, the kernel $\mathcal{K}$ and the function $\mathcal{Q}$. If we express the exchange potential as a linear combination of basis functions, Eq. 34 can be rewritten as a non-homogeneous set of linear equations for the coefficients of the expansion of the potential in the basis set. More details on the separation procedure can be found in Ref. [62].

5. SYSTEMS STUDIED AND CORRESPONDING DENSITIES

Experimental and computed energies are often compared in order to assess the accuracy of approximate density functionals. However, this procedure is not very reliable since energies are integrated quantities and are therefore subject to cancellation of errors. In order to better understand the performance of approximate exchange-correlation functionals, we will examine not only total energies but also the components of the energy, the self-consistent charge densities, the exchange-correlation potentials and the local exchange energies per electron. We will compare these quantities, obtained from approximate schemes, with the corresponding accurate quantities derived from (1) the exact solution of a model system of two interacting electrons in a harmonic potential (we call this system "Harmonium"), (2) a nearly exact wave function for the He atom and (3) accurate quantum Monte Carlo calculations for the Be and Ne atoms.

5.1. Harmonium

A simple two-electron system where the exchange-correlation potential and energy is calculable exactly consists of two interacting electrons in a harmonic potential. The model can be solved analytically for a discrete and infinite set of values of the spring constant k [63] and the degree of correlation within the system can be varied by simply tuning the value of k.

In Fig. 1, we show the density in a low correlation case, corresponding to a spring constant $k = 0.25$ a.u., and in a high correlation case with a spring constant $k \approx 3.6 \times 10^{-6}$ a.u. In the low correlation case, the density has a maximum at the origin while, in the high correlation case, the density has a local minimum at the origin and an absolute maximum at a finite distance from the origin [54]. Although the high correlation density is too low to be physically relevant for electronic structure calculations ($\langle r_s \rangle = 57.9$ a.u.), the system is interesting because it is strongly correlated and its density differs qualitatively from an atomic density due to the presence of a maximum at a finite distance from the origin. Consequently, in the present paper, we will only discuss the high correlation limit. For an analysis of the system with $k = 0.25$ a.u., see Ref. [54].

5.2. He atom

It is necessary to employ very accurate wave functions in order to observe the true short-distance and long-distance behavior to $\mathcal{O}(1/r)$ of the exchange-correlation potential.

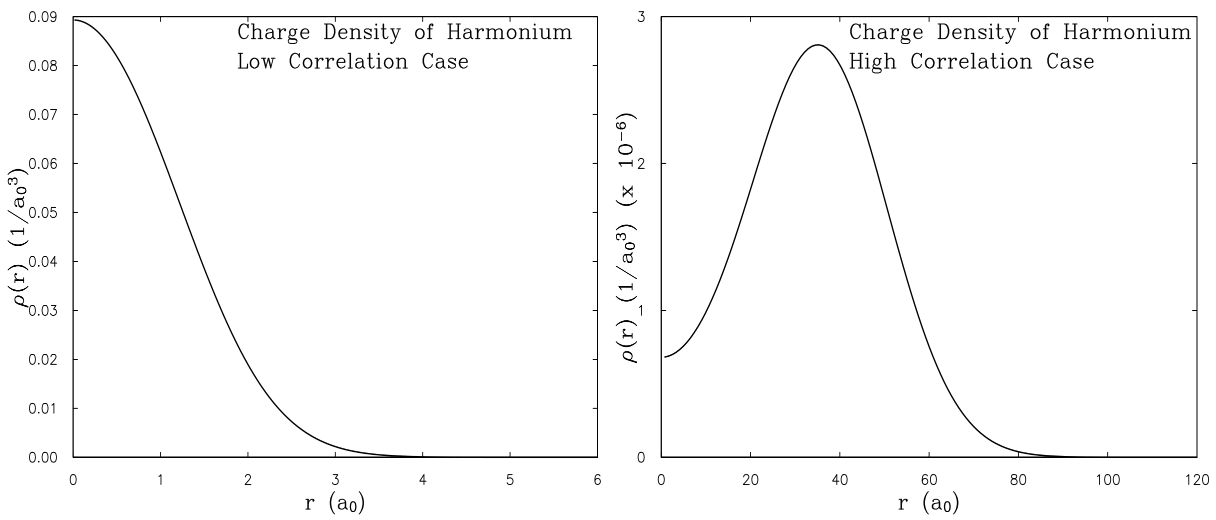

Figure 1. Ground state electronic densities: the spring constants are $k = 0.25$ a.u. (left, low correlation case) and $k \approx 3.6 \times 10^{-6}$ a.u. (right, high correlation case). Taken from Ref. [54] and modified.

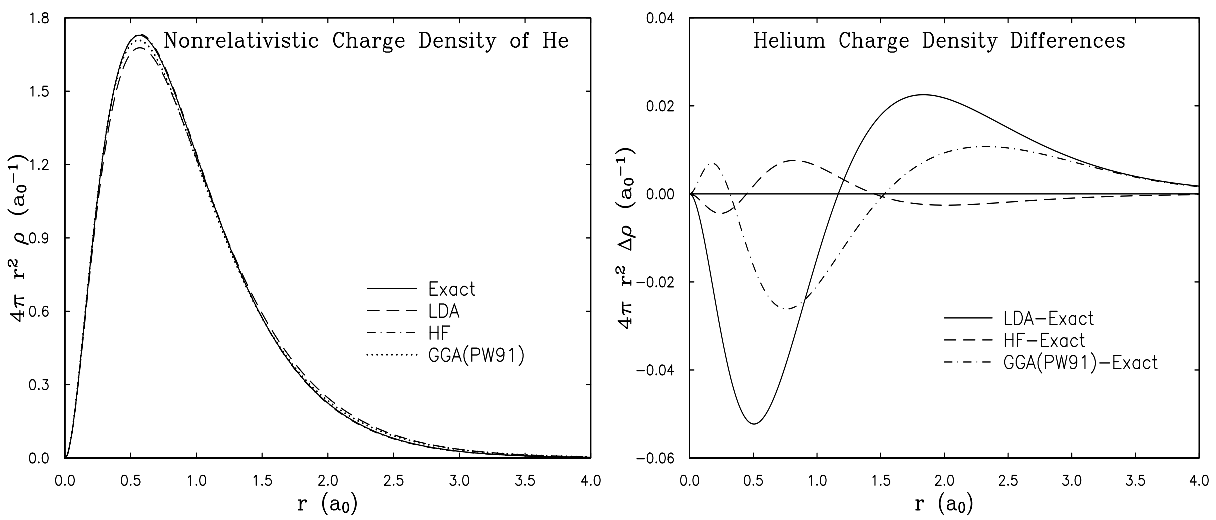

Figure 2. Comparison of the LDA, GGA (PW91), HF and exact densities of He (left). Errors in the LDA, GGA, and HF densities of He (right). Taken from Ref. [55] and modified.

For the He iso-electronic series, it is possible to achieve this accuracy. The form of the wave function is described in Refs. [55,64]. The energy for He corresponding to this wave function was estimated to be about 1 part in 10^{16}. With this nearly exact wave function, the exchange-correlation potential is resolved with unprecedenced accuracy: it is possible to observe [55] not only the $-1/r$ behavior of the exchange potential but also the asymptotic behavior of the correlation potential, $-9/(4Z^4r^4)$, predicted by Almbladh and von Barth [65].

In Fig. 2, we compare the density obtained with our accurate wave function with the self-consistent densities obtained from LDA, the Perdew-Wang '91 GGA[14] and Hartree-Fock (HF). The LDA density is less peaked than the true density while the HF density is very close but slightly more peaked than the true density. We also show the error in the LDA, GGA, and HF densities. The GGA density is more accurate than the LDA density but less accurate than the HF one. Note that the error in the HF density is considerably smaller than the LDA and GGA errors; however, as shown below, this is true only in the core region for heavier systems.

5.3. Be atom

For many-electron systems, an accurate determination of the charge densities is obtained by combining the results from variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC) methods [66]. In VMC, the square of a trial wave function is sampled and the expectation values for the trial wave function are calculated as averages over the sampled configurations. An advantage of this technique versus other conventional quantum chemistry methods is that the many-dimensional integrals can be performed for any given form of the trial wave function. Therefore, one is freed from the constraint of having to express the trial wave function in some restricted form such as a linear combination of determinants of single-particle orbitals. The starting point of the DMC method is also a good trial wave function from which DMC projects out an improved estimate of the true wave function.

To calculate the charge density, the integral of the square of the true wave function over all but one of the electrons has to be estimated. VMC samples the square of the trial wave function. DMC samples the product of the trial wave function and the true wave function. If the error in the wave function is of $\mathcal{O}(\epsilon)$, the errors in the densities obtained from VMC and DMC are of the same order. A density with an error of $\mathcal{O}(\epsilon^2)$ (that we will refer to as the quantum Monte Carlo (QMC) density) is obtained by taking twice the DMC density and subtracting the VMC density[67]. The QMC density is obtained in the form of an histogram and then fitted to a sum of products of monomials, exponentials and an appropriate asymptotic function [68].

In Fig. 3, we show the densities (left) obtained from LDA, the Perdew-Wang '91 GGA, HF and QMC for Be and the errors in these densities (right), with the QMC density as the reference. The first thing to notice is that all densities are very similar. The LDA and HF errors are of comparable magnitude in the valence region whereas, as in the case of He (Fig. 2), the HF error is smaller than the LDA error in the region near the nucleus. A hand-waving explanation of this behavior is that, in the core region, exchange dominates correlation and HF, by definition, is exact for exchange only. The Perdew-

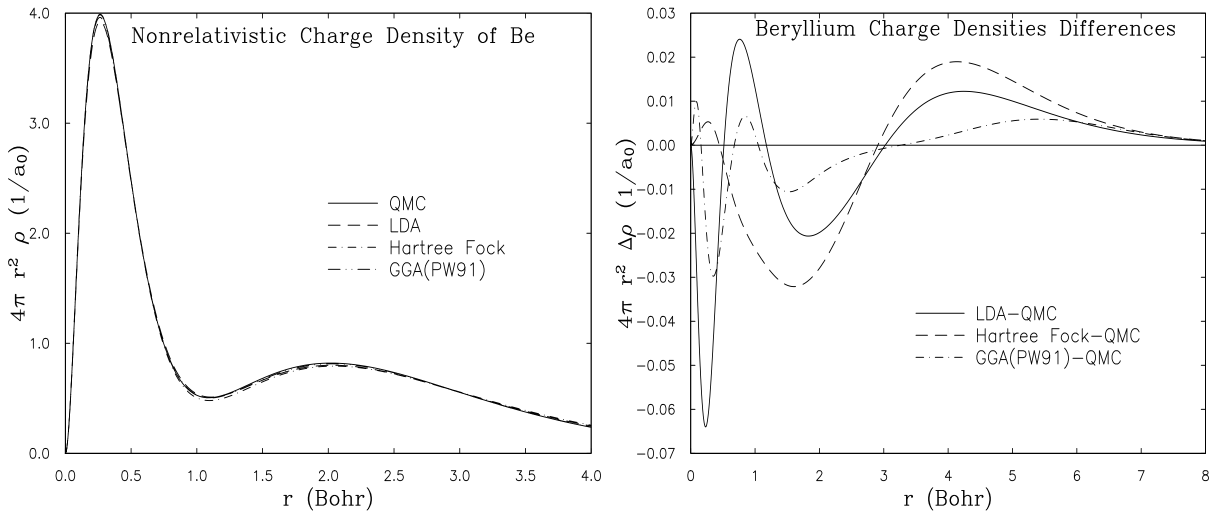

Figure 3. Comparison of the LDA, GGA (PW91), HF and "exact" (QMC) densities of Be (left). Errors in the LDA, GGA, and HF densities of Be (right). Taken from Ref. [47].

Wang '91 density is somewhat more accurate than the LDA density. The GGA potential has a spurious negative divergence at the nucleus that is partially responsible for the improvement in the density. The LDA density is too low at the nucleus and the negative divergence of the GGA potential results in increased charge density there, a feature we have observed for Ne as well.

6. A CLOSER LOOK AT EXISTING APPROXIMATIONS: $v_{\rm XC}$, $v_{\rm X}$ AND $v_{\rm C}$

The accurate exchange-correlation potentials and their separation in exchange and correlation components were obtained for the four systems described in this paper, using the techniques mentioned in Sec. 4. The approximate exchange-correlation potentials are evaluated numerically as functional derivatives of the approximate exchange-correlation energy functionals (Eq. 16) and compared with the corresponding accurate quantities.

6.1. Harmonium

In Fig. 4, we plot the exact exchange potential and several approximate exchange potentials evaluated for the exact density of the model system. The approximate potentials differ from the exact potential over all the spatial range. At large r, all the potentials do not reproduce the correct $-1/r$ asymptotic behavior: they go exponentially to zero with the exception of the Becke functional which behaves as $(-\text{constant}/r^2)$ [18] and of the Langreth-Mehl functional which diverges. At the origin, the exact exchange potential has a minimum because it is simply proportional to the Hartree potential through Eq. 29 while the approximate exchange potentials exhibit a maximum (they do not diverge since, from Eq. 19, $s = 2$ and $m > 1$). The Perdew-Wang '91 exchange potential is very close to the Becke '88 potential except that it displays additional oscillations at the extrema

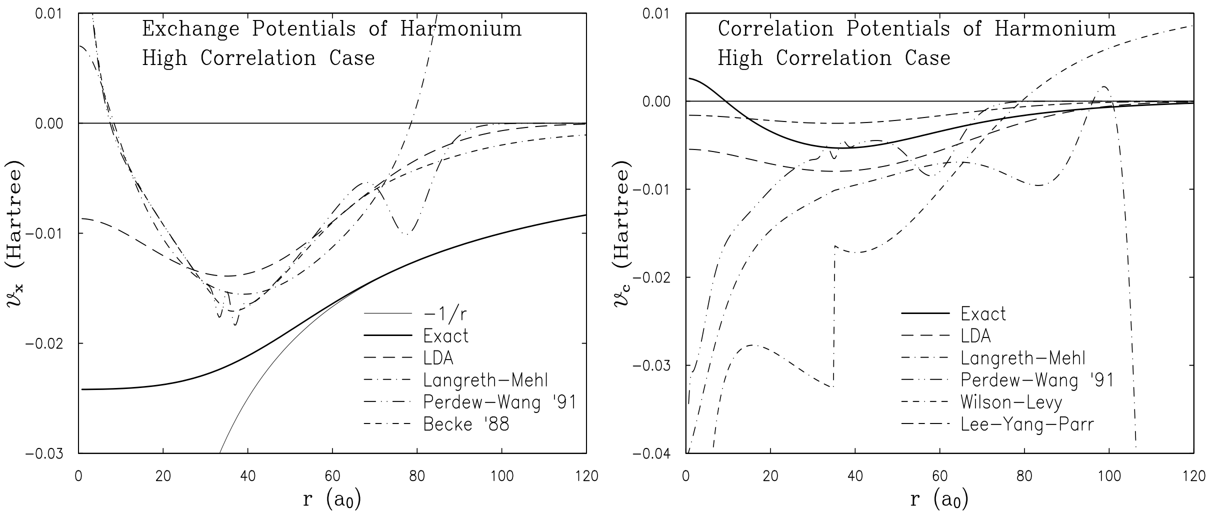

Figure 4. Exact and approximate exchange (left) and correlation (right) potentials for the spring constant $k \approx 3.6 \times 10^{-6}$ a.u. Taken from Ref. [54] and modified.

of the densities and in the tail of the density. In addition, as mentioned earlier, the long-distance asymptotic behaviors are different. As pointed out by Engel and Vosko [69], the oscillations of the Perdew-Wang '91 potential at the quadratic extrema of the density are due to the fact that the effective coefficient of the $|\nabla\rho|^2$ term increases very rapidly from the known value at $\xi = 0$, specified by the second-order gradient expansion, to a 2.1 times larger value at only $\xi = 0.04$, where $\xi = [\nabla\rho/(2k_F\rho)]^2$ and k_F is the Fermi wave vector. Observe that the Becke '88 potential does not have spurious oscillations at the extremum of the density nor in the tail of density.

In Fig. 4, we also show the exact correlation potential and several approximate correlation potentials evaluated for the exact density. At large r, the approximate potentials go to zero exponentially with the exception of the Wilson-Levy potential which goes to a positive constant and the Langreth-Mehl functional which diverges. As predicted by Eq. 19, the Wilson-Levy potential diverges at the origin: the energy density, $e_{\rm xc}(\rho, |\nabla\rho|)$, depends on $|\nabla\,\rho|$ as $\mathcal{O}(|\nabla\rho|)$ for small values of the gradient of the density (Eq. 19, $m = 1$). All the other functionals assume a finite value at the origin (Eq. 19, $s = 2$ and $m > 1$). The Wilson-Levy functional has a discontinuity at the maximum of the electronic density: the functional derivative of the exchange-correlation energy contains the sign of the radial derivative of the density and is discontinuous if the energy density depends on the absolute value of gradient of the density as $\mathcal{O}(|\nabla\rho|)$, for small values of $|\nabla\rho|$. As in the case of exchange the Perdew-Wang '91 correlation potential shows an oscillatory behavior near the maximum at a finite distance from the origin and also in the tail of the potential.

6.2. He atom

For atomic systems, the exchange potential is the dominant part of the exchange-correlation potential. It shares with it most of its characteristics: the asymptotic behavior, the intershell bump (see Sub-sec. 6.3) and the finite short-range behavior.

In Fig. 5 we compare the exchange potential obtained from the LDA and the various GGA's evaluated for the exact charge density with the exact potential obtained from Eq. 29. The approximate potentials differ significantly from the exact one. At large r, all the potentials do not reproduce the correct $-1/r$ asymptotic behavior: they go exponentially to zero with the exception of the Becke '88 functional which behaves as $(-\text{constant}/r^2)$ [18] and of the Langreth-Mehl functional which diverges. The Perdew-Wang '91 functional has a spurious minimum between 2.5 and 3.5 a_0.

At the origin, the exact exchange potential has a quadratic minimum because it is simply proportional to minus the Hartree potential. In contrast all the proposed GGA exchange potentials diverge at the nucleus while the LDA exchange potential has a finite value and slope there. Hence, very close to the nucleus, the various GGA potentials are an even poorer approximation to the true potential than LDA but the more negative values of the GGA potentials at short and intermediate distances is a step in the right direction. As shown in Eq. 19, any approximate functional that has terms containing the gradient but no higher derivatives of ρ must yield an exchange-correlation potential that diverges at nuclei since, at nuclei, $s = 1$.

In Fig. 5, we also compare approximate correlation potentials of He to the exact one. In the case of an n-electron atom or ion with orbitally non-degenerate n and $n-1$ electron ground states, the correlation potential goes as $-\alpha/2r^4$ at large distances, where α is the dipole-polarizability of the $n-1$ electron system[65]. In the case of the He iso-electronic series, the dipole-polarizability of the residual 1-electron system is $\alpha = 9/(2Z^4)$. Due to the rapid fall-off of $1/r^4$, this asymptotic behavior is not discernible in Fig. 5 but is evident in a plot of $r^4 v_c$ [55]. At large distances, the approximate potentials go to zero exponentially with the exception of the Wilson-Levy potential which goes to a positive constant and the Langreth-Mehl potential which diverges. All the GGA correlation potentials diverge at the origin as follows from Eq. 19. Of the GGA's proposed so far, only the Lee-Yang-Parr GGA contains Laplacian terms but not in the form necessary to eliminate the divergence at the nucleus.

6.3. Be and Ne atoms

In Fig. 6, we show the accurate exchange potentials of Be and Ne and compare them with the approximate exchange potentials from the local density approximation and several generalized gradient approximations, all of them being evaluated for the corresponding accurate QMC density.

At short and large distances, all GGA's are similar and qualitatively wrong and the same analysis applies as in the case of the He atom. The Perdew-Wang '91 exchange potential has a spurious dip at about 6 a.u. (outside the plotted range) for Be and at about 3.3 a.u. for Ne. This dip is not present in either Perdew-Wang '86 or the Becke '88 potentials. The exact exchange potential has a peak in the intershell region (around 1 a.u. for Be and around 0.3 a.u. for Ne). There, the various GGA potentials exhibit some differences

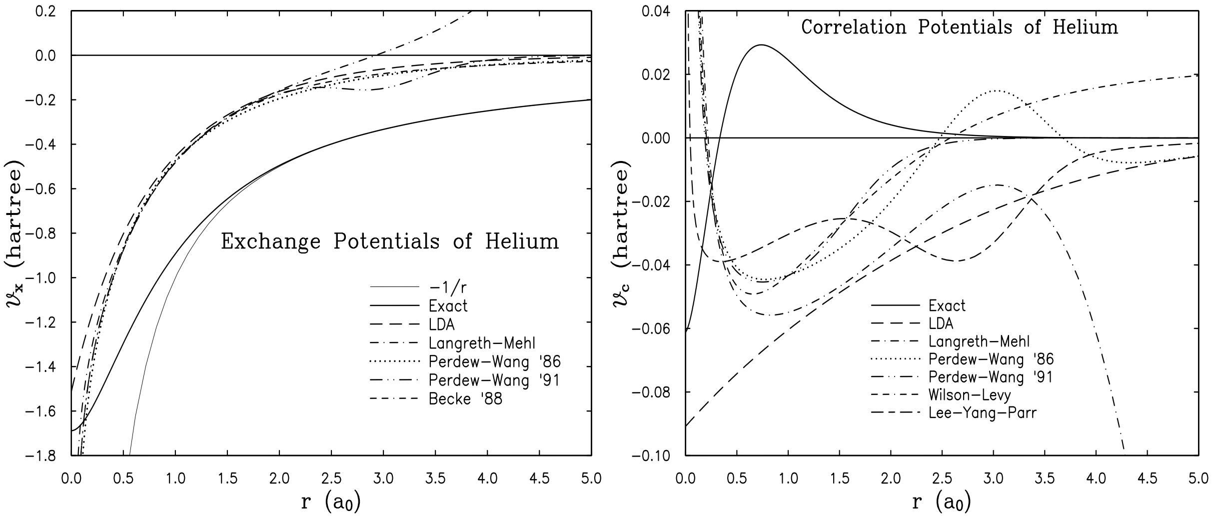

Figure 5. Exact and approximate exchange (left) and correlation (right) potentials for He. Taken from Ref. [55] and modified.

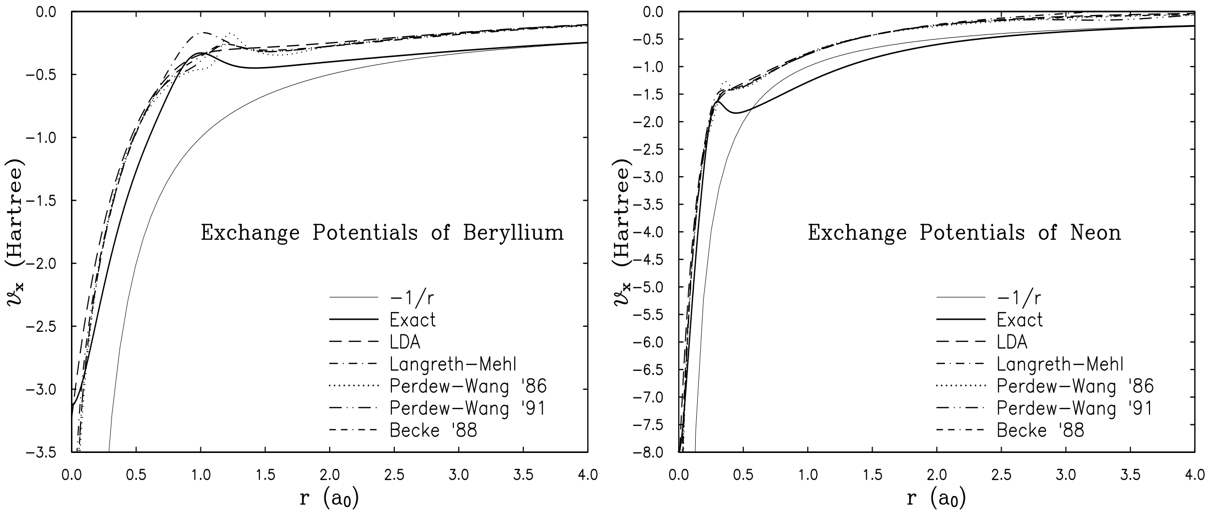

Figure 6. Exchange potentials of Be (left) and Ne (right) from QMC (labeled exact - see text), LDA and various GGA's. Taken from Ref. [47].

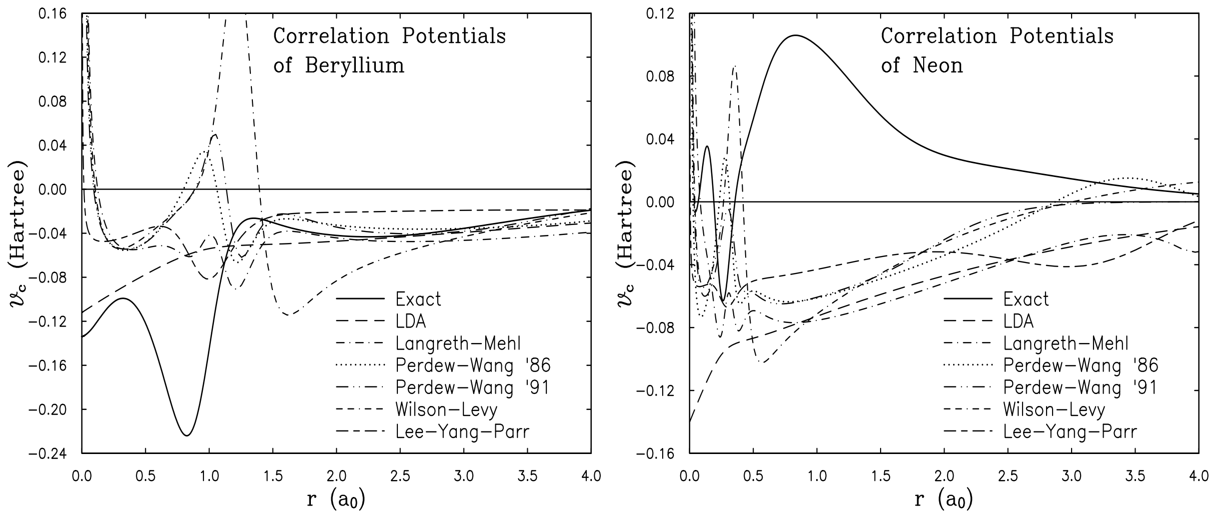

Figure 7. Correlation potentials of Be (left) and Ne (right) from QMC (labeled exact - see text), LDA and various GGA's. The "exact" Ne potential has significant uncertainty for $r < 0.4\ a_0$. Taken from Ref. [47].

but they all have a peak at approximately the right position. The GGA potentials are more accurate than the LDA potential at distances smaller than the intershell radius, except at very short distances where they have a spurious divergence. To summarize, the exchange potentials from the GGA's show some tendency for improvement upon LDA in the intershell region and at shorter distances but they have a spurious divergence at the nucleus and do not improve the long-distance behavior.

In Fig. 7, we show the correlation potentials for Be and Ne from QMC, LDA and the different GGA's. The LDA correlation potential is everywhere negative, monotonically increasing with the radius (since the density is monotonically decreasing) and rather smooth. Except for the part of the potential beyond 1.5 a.u. for Be, it bears no resemblance to the exact correlation potential. The GGA correlation potentials exhibit more structure but none of these does better than LDA. Nevertheless, as we will see in Section 8 the GGA's yield more accurate correlation energies than does LDA. The true correlation potential is everywhere negative for Be but is predominantly positive for Ne.

7. LOCAL EXCHANGE ENERGY PER ELECTRON: ϵ_{X}

Using the expression in Eq. 25 for the local exchange energy per electron, ϵ_{x}, we present accurate ϵ_{x}'s for the two-electron systems and the Be atom. Since ϵ_{x} is not uniquely defined (see Sec. 4), the differences of approximate ϵ_{x}'s from each other and from the "true" one are not necessarily indicative of a failure of the approximate functionals.

In the left panel of Fig. 8, we plot the exact and approximate local exchange energies per electron for Harmonium. At large r, the approximate exchange functionals go to zero exponentially with the exception of the Langreth-Mehl functional which diverges and of

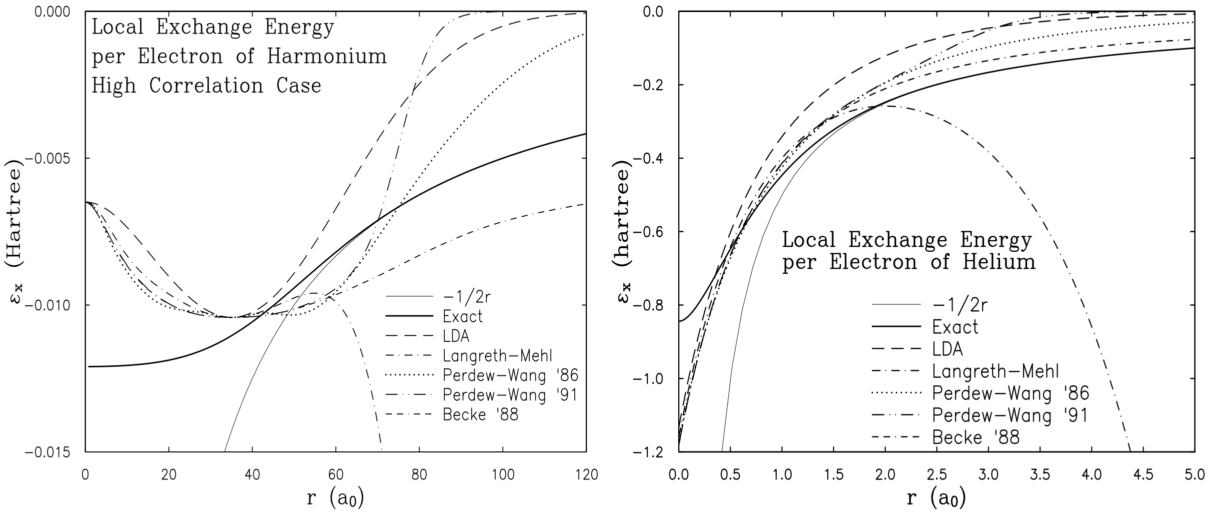

Figure 8. Exact and approximate local exchange energy per electron for Harmonium ($k \approx 3.6 \times 10^{-6}$ a.u.) (left) and He (right), evaluated for the respective exact densities. Taken from Refs. [54] and [55] and modified.

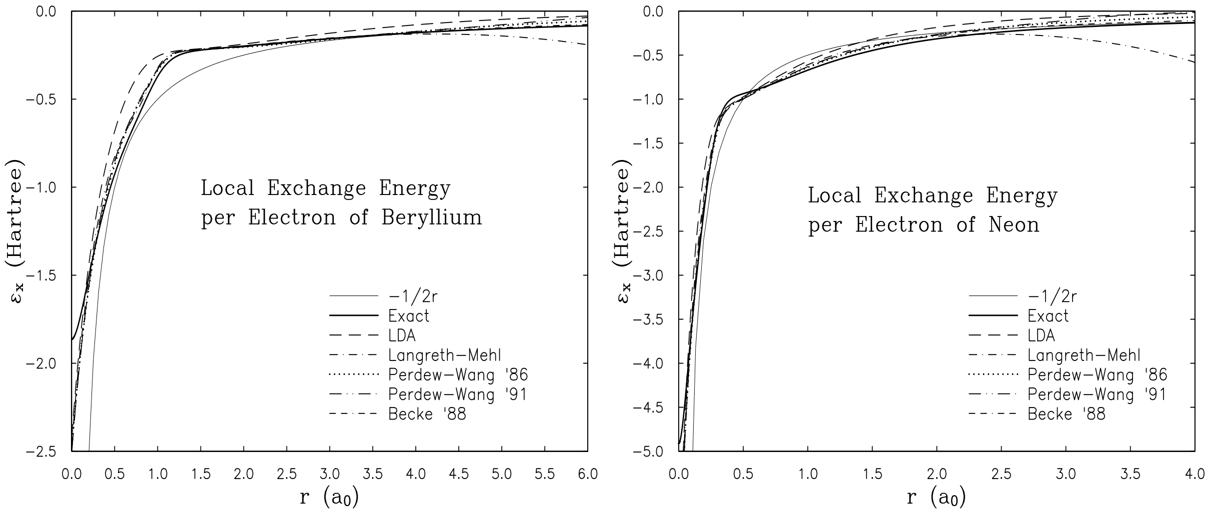

Figure 9. Exact and approximate local exchange energy per electron for Be (left) and Ne (right), evaluated for the respective exact densities.

the Becke functional which has the wrong asymptotic behavior $-1/r$ for Harmonium although it has the correct asymptotic behavior $-1/2r$ for atoms. The Becke functional was constructed to have the correct asymptotic behavior for exponentially decaying density but it fails for Gaussian densities (see Table 1). At the extrema of the density, all the functionals go to the LDA value.

In the right panel of Fig. 8 and in Fig. 9, we compare the exact and approximate local exchange energies per electron of the He, Be and Ne atoms. At large r, the approximate $\epsilon_{\rm x}$ go to zero exponentially with the exception of the Langreth-Mehl functional, which diverges, and the Becke functional which has the correct asymptotic behavior $-1/2r$. However, as also noted by Engel *et al.* [18], the Becke $\epsilon_{\rm x}$ achieves its asymptotic behavior at much larger distances than does the true $\epsilon_{\rm x}$. This is because the correction to the leading $-1/2r$ term is exponentially small for the true functional but $\mathcal{O}(1/r^2)$ for the Becke functional. The Becke exchange energy per electron is however closer to the correct one over all the range than any other approximate $\epsilon_{\rm x}$. At intermediate distances, the various GGA's represent an improvement upon LDA, yielding a deeper $\epsilon_{\rm x}$ than LDA, but, at very short distances, they are significantly lower than the true one.

8. COMPARISON OF THE COMPONENTS OF THE TOTAL ENERGY

For the model system of two electrons in a harmonic potential, the He iso-electronic series and the Be atom, we present a comparison of the accurate values of $E_{\rm x}$, $E_{\rm c}$ and $E_{\rm xc}$ with the ones corresponding to approximate functionals evaluated for the accurate densities. In order to assess the change that results from employing the self-consistent rather than the exact density, we also perform, for Be, self-consistent calculations with LDA and the Perdew-Wang '91 GGA and compare the different components of the total energy (Eq. 6) with the accurate values.

For the model system of two interacting electrons in a harmonic potential, we compare in Table 2 the values of the exact exchange and correlation energies with those obtained from the approximate functionals evaluated for the exact electronic density. The GGA functionals, except for the Langreth-Mehl functional, improves considerably upon LDA. The major corrections are achieved for the exchange contribution. The failure of the Langreth-Mehl functional is a result of the diverging energy per electron at large r. Most of the approximate functionals are constructed to give accurate values of $E_{\rm xc}$ for atoms and it is encouraging that they also improve $E_{\rm xc}$ for this rather different model system. However, we can see in Tables 3 and 4 that the improvement upon LDA is much larger for atomic systems: for instance, the percentage error in the LDA exchange energy evaluated for the electronic density of He is 14% and in the LDA correlation energy, -165%, while the percentage errors for the other approximate functionals we list in the appendix range from -1 to 1% for exchange and from -3 to 19% for correlation. If we consider the sum of the exchange energy and the correlation energy, LDA yields a good result due to a cancellation of errors and the GGA's do not improve upon LDA.

In Tables 3 and 4, we compare the approximate $E_{\rm x}$, $E_{\rm c}$ and $E_{\rm xc}$, evaluated for the accurate densities of the He iso-electronic series and Be respectively, with the corresponding accurate quantities. As is well known, LDA yields values of $E_{\rm x}$ that are too small in

Table 2
Model system with spring constant $k \approx 3.6 \times 10^{-6}$ a.u. Exchange-correlation energy for the approximate functionals listed in Appendix A. The functionals are evaluated for the exact density. The exact results are also reported. The numbers in parentheses are the percentage errors. The total energy of the system is 0.0228 a.u. Energies are in Hartree atomic units. Taken from Ref. [54] and modified.

Functional	E_x	E_c	E_{xc}
Exact KS	−0.0195	−0.0064	−0.0259
LDA (Perdew-Wang)	−0.0174(11%)	−0.0108(−69%)	−0.0282(−9%)
Langreth-Mehl	−0.0217(−11%)	−0.0119(−86%)	−0.0336(−30%)
Perdew-Wang '86	−0.0198(−2%)	−0.0096(−50%)	−0.0294(−14%)
Perdew-Wang '91	−0.0195(0.2%)	−0.0084(−31%)	−0.0279(−8%)
Becke '88	−0.0201(−3%)	—	—
Wilson-Levy	—	−0.0145(−127%)	—
Lee-Yang-Parr	—	−0.0032(50%)	—

absolute magnitude and values of E_c that are too large in absolute magnitude, resulting in a cancellation of errors for E_{xc}. All the GGA's yield improved exchange, correlation and exchange-correlation energies compared to the LDA.

For the He iso-electronic series, the true correlation energies are nearly constant, whereas for the Be iso-electronic series there is a linear component in the nuclear charge Z. It is difficult for any GGA functional to mimic the correct Z dependence of both iso-electronic series.

In Table 5, we show various quantities, computed by LDA and the Perdew-Wang '91 GGA, and the corresponding accurate values for Be. LDA and GGA values were obtained through a self-consistent procedure and are therefore evaluated for the LDA and the GGA density respectively. The change in E_x and E_c due to self-consistency are not negligible. The values of E_x and E_c in Table 5 differ from those in Table 5 by a larger amount for LDA than for the Perdew-Wang '91 GGA reflecting our earlier observation that the GGA yields somewhat more accurate self-consistent densities than does LDA. The last two columns show the errors in LDA and GGA. The LDA components of the total energy are all smaller in absolute magnitude than the corresponding accurate values. Both the total energy and its components have much smaller errors in GGA than in LDA. In Fig. 3, we observed that, near the nucleus, the LDA density is too small while GGA gives an increased charge density due to the lower value at short distances and the negative divergence at the nucleus of the GGA exchange-correlation potential. This increase in the GGA density results in an increase in the magnitude of all the components of the total energy. Consequently, the GGA yields improvements not only in E_{xc} but also in other components of the total energy, despite, or may be one should say because of, the spurious divergence of the exchange-correlation at the nucleus. On the other hand, quantities related to the single-particle eigenvalues (shown in the last two rows) are not improved in GGA relative to LDA. In particular, the highest lying eigenvalue which, for the true density functional, should equal the ionization energy, is not much improved.

Table 3: Comparison of exchange and correlation energies of the He iso-electronic series for LDA and the various GGA's with the corresponding exact values. The approximate functionals are evaluated for the exact (not the self-consistent) densities. The numbers in parentheses are the percentage errors. All numbers are accurate to all digits presented with the exception of the "exact" results for Hg^{+78} which probably have an error in the last digit. Taken from Ref. [55] and modified.

	Ion	Exact	LDA [15]	LM [9]	PW86 [12,13]	PW91 [14]	B88 [11]	WL [16]	LYP [17]
	H^-	−0.380898	−0.337(12%)	−0.387(−2%)	−0.400(−5%)	−0.393(−3%)	−0.395(−4%)	—	—
	He	−1.024568	−0.883(14%)	−1.014(1%)	−1.033(−1%)	−1.016(1%)	−1.025(−0%)	—	—
E_x	Be^{+2}	−2.276628	−1.957(14%)	−2.246(1%)	−2.279(−0%)	−2.245(1%)	−2.265(1%)	—	—
	Ne^{+8}	−6.027484	−5.173(14%)	−5.940(1%)	−6.015(0%)	−5.927(2%)	−5.982(1%)	—	—
	Hg^{+78}	−49.777931	−42.699(14%)	−49.036(1%)	−49.605(0%)	−48.889(2%)	−49.348(1%)	—	—
	H^-	−0.041995	−0.072(−71%)	−0.049(−16%)	−0.038(10%)	−0.032(24%)	—	−0.032(25%)	−0.030(29%)
	He	−0.042107	−0.112(−167%)	−0.050(−19%)	−0.044(−4%)	−0.046(−9%)	—	−0.042(1%)	−0.044(−4%)
E_c	Be^{+2}	−0.044274	−0.150(−240%)	−0.025(43%)	−0.049(−12%)	−0.053(−21%)	—	−0.045(−2%)	−0.049(−11%)
	Ne^{+8}	−0.045694	−0.202(−342%)	0.082(279%)	−0.084(−83%)	−0.062(−35%)	—	−0.047(−3%)	−0.050(−10%)
	Hg^{+78}	−0.046538	−0.326(−600%)	1.833(4038%)	−0.299(−543%)	−0.081(−73%)	—	−0.048(−3%)	−0.051(−9%)
	H^-	−0.422893	−0.408(3%)	−0.435(−3%)	−0.438(−4%)	−0.425(−0%)	—	—	—
	He	−1.066675	−0.996(7%)	−1.064(0%)	−1.077(−1%)	−1.062(0%)	—	—	—
E_{xc}	Be^{+2}	−2.320902	−2.107(9%)	−2.271(2%)	−2.328(−0%)	−2.298(1%)	—	—	—
	Ne^{+8}	−6.073178	−5.375(11%)	−5.858(4%)	−6.099(−0%)	−5.989(1%)	—	—	—
	Hg^{+78}	−49.824470	−43.025(14%)	−47.203(5%)	−49.904(−0%)	−48.970(2%)	—	—	—

Table 4
Comparison of exchange and correlation energies of Be for LDA and the various GGA's with the corresponding accurate values. The approximate functionals are evaluated for the exact (not the self-consistent) densities. The numbers in parentheses are the percentage errors. Energies are in Hartree atomic units. Taken from Ref. [47].

Functional	E_{x}	E_{c}	E_{xc}
Accurate	−2.67398	−0.09615	−2.77013
LDA (Perdew-Wang)	−2.32125(13%)	−0.22515(−134%)	−2.54641(8%)
Langreth-Mehl	−2.60576(3%)	−0.10012(−4%)	−2.70588(2%)
Perdew-Wang '86	−2.69050(−1%)	−0.09425(2%)	−2.78475(−1%)
Perdew-Wang '91	−2.65434(1%)	−0.09496(1%)	−2.74929(1%)
Becke '88	−2.66694(0%)	—	—
Wilson-Levy	—	−0.09572(0%)	—
Lee-Yang-Parr	—	−0.09546(1%)	—

Table 5
Comparison of LDA, Perdew-Wang '91 GGA and accurate values for various components of the Kohn-Sham total energy, the density-weighted integral of v_{xc} and single-particle eigenvalues of Be. The approximate functionals are evaluated for the respective self-consistent densities. The accurate values probably have errors in the last digit quoted. The accurate value of the total energy is from Ref. [70]. Energies are in Hartree atomic units. Taken from Ref. [47].

Property	LDA	PW91	Accurate	Δ_{LDA}	Δ_{PW91}
$E = T_{\mathrm{s}} + E_{\mathrm{en}} + E_{\mathrm{H}} + E_{\mathrm{xc}}$	−14.44647	−14.64794	−14.66736	0.22089	0.01942
T_{s}	14.30879	14.57461	14.5942	−0.2854	−0.0196
E_{en}	−33.35610	−33.65670	−33.7099	0.3538	0.0532
E_{H}	7.11487	7.17261	7.2185	−0.1036	−0.0459
E_{xc}	−2.51403	−2.73845	−2.77013	0.25610	0.03168
E_{x}	−2.29033	−2.64428	−2.67398	0.38365	0.02970
E_{c}	−0.22370	−0.09417	−0.09615	−0.12754	0.00198
$E_{\mathrm{en}} + E_{\mathrm{H}}$	−26.24123	−26.48410	−26.4914	0.2502	0.0073
$\int d\mathbf{r}\, \rho(\mathbf{r})\, v_{\mathrm{xc}}(\mathbf{r})$	−3.30614	−3.50058	−4.4595	1.1533	0.9589
ϵ_{1s}	−3.85609	−3.91154	−4.2265	0.3704	0.3149
ϵ_{2s}	−0.20577	−0.20719	−0.3426	0.1368	0.1354

This is to be expected since the long-distance behavior of exchange-correlation potential, which strongly influences the highest eigenvalue, is not appreciably improved. All the observations made here for the Be atom are also true for the Ne atom (see Refs. [45] and [47]).

9. PROSPECTS

Although the exchange and correlation energies calculated from the various GGA's (with the exception of the Langreth-Mehl GGA for the model system and for the correlation energies in the He iso-electronic series) are considerably more accurate than those from LDA, the situation is not as clear for the exchange and correlation potentials. Since E_{x} and E_{c} are integrated quantities, it is possible for GGA's to improve upon them without making comparable improvements to the exchange and correlation potentials which contain more detailed information.

The various GGA exchange functionals have certain features in common. By favoring regions with large density gradients, they correctly lead to more negative total energies and reduced binding energies relative to LDA. They yield a lower potential than LDA at short and intermediate distances from nuclei and approximately reproduce the intershell structure – two steps in the right direction – but they also introduce a spurious divergence at the nucleus and fail to improve the long-range behavior. Whereas the various GGA exchange functionals have some common features, the GGA correlation functionals are very different from each other and none of them yields a correlation potential resembling the true one. Correlation is more subtle than exchange as manifested in several ways. 1) The exchange potential is everywhere negative, whereas the correlation potential can be either negative or positive in different regions of space. 2) For He iso-electronic series, the correlation potential varies less over space for heavy ions than for light atoms [55]. This is opposite to the behavior in LDA. 3) The correlation potential has qualitatively the same behavior for all members of the helium iso-electronic series [55] (negative at short distances and long distance, positive at intermediate distances, see Fig. 5) but it has the opposite qualitative behavior for the closely related model system of two electrons in a harmonic potential (Fig. 4).

As discussed in Sec. 2, any GGA that includes no higher than first derivatives of the density cannot simultaneously satisfy both the correct $-1/r$ behavior of the exchange-correlation potential and the correct $-1/2r$ behavior of exchange energy per electron at large distances. Moreover, any such GGA must have a spurious divergence in the exchange-correlation potential at nuclei. We mentioned that, by including the Laplacian of the density in an appropriate way, it is possible to construct a GGA that has the correct long-range asymptotics of the exchange potential and energy per electron and the proper short-range behavior of the exchange-correlation potential. Nevertheless, it may turn out that even GGA functionals containing Laplacian terms are not flexible enough to achieve a major improvement and it may be necessary to consider more general functionals. We discuss here some possibilities.

Since a data-base on accurate exchange-correlation potentials has being built in recent years and none of the existing GGA functionals passes the test of the comparison with the true potentials, more effort is now being devoted to developing schemes that focus on reproducing the main features of the true exchange-correlation potential. As mentioned above, the potential controls the quality of the self-consistent density and is the key ingredient in evaluating energy gradients [71],

$$\frac{\partial E_{\mathrm{xc}}[\rho]}{\partial \mathrm{X}} = \int v_{\mathrm{xc}}([\rho];\mathbf{r}) \frac{\partial \rho(\mathbf{r})}{\partial \mathrm{X}} \, \mathrm{d}\mathbf{r}, \tag{37}$$

whose accurate estimation is for instance necessary in determining potential energy surfaces.

Instead of starting from an exchange-correlation energy functional and then deriving the corresponding potential, some authors start with an expression for the potential which has the correct asymptotic behavior [39,73]. While it is easy to construct a potential with the correct asymptotics, one encounters the problem of how to obtain the exchange-correlation energy functional that corresponds to this potential. In fact, the potential may not be the functional derivative of an energy expression. If the approximate exchange potential satisfies the uniform scaling property $v_{\mathrm{x}}([\rho_\lambda];\mathbf{r}) = \lambda v_{\mathrm{x}}([\rho];\lambda\mathbf{r})$, a possibility is to use the Levy-Perdew relation to assign a corresponding exchange energy [50]:

$$E_{\mathrm{x}} = \int v_{\mathrm{x}}([\rho];\mathbf{r}) \left(3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})\right) \mathrm{d}\mathbf{r}. \tag{38}$$

The relation is derived by considering a line integral of the potential along the density path ρ_λ (Eq. 11) and is exact only for a potential that is a functional derivative and has the correct scaling property:

$$E_{\mathrm{x}}[\rho] = \int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{r}\; v_{\mathrm{x}}([\rho_\lambda];\mathbf{r}) \frac{\mathrm{d}\rho_\lambda(\mathbf{r})}{\mathrm{d}\lambda} = \int v_{\mathrm{x}}([\rho];\mathbf{r}) \left(3\rho(\mathbf{r}) + \mathbf{r}\cdot\nabla\rho(\mathbf{r})\right) \mathrm{d}\mathbf{r}. \tag{39}$$

The first equality always holds for a potential that is a functional derivative while the second one is valid only if the potential has the correct behavior under uniform scaling. Van Leeuwen and Baerends [71] discuss why Eq. 38 is a sensible choice for a potential that is not a functional derivative but has the proper scaling property and is constructed to mimic the true potential at the given density. Unfortunately, such a relation does not exist in the case of exchange and correlation since the scaling properties of the correlation potential are not homogeneous [49]. Assigning an exchange-correlation energy to a given potential becomes more complicated because we need to know the potential not only for the density of interest, as in the case of exchange-only, but along some path in density space [71].

Another attempt to generate a DFT scheme yielding a better description of the exchange-correlation potential has as a starting point the OEP method. The OEP method provides the exact solution for the problem of exchange-only DFT but, as shown by Norman and Koelling [72], it can be generalized to treat exchange and correlation if the correlation energy is also expressed as a functional of the Kohn-Sham orbitals. The resulting problem is technically difficult to solve but Krieger, Li and Iafrate proposed an approximation that greatly simplify the approach [74]. Although the resulting exchange-correlation potential is no longer equivalent to the functional derivative with respect to the density of the original exchange-correlation energy, it closely corresponds to the exact generalized OEP exchange-correlation potential if the expression $\delta E_{\rm xc}\left[\{\psi_i\}\right]/\delta\psi_i(\mathbf{r})/\psi_i^*(\mathbf{r})$ goes to zero at large distances. Since the true exchange energy is known as a functional of the Kohn-Sham orbitals (Eq. 21) and can therefore be employed, the approximate exchange potential, evaluated according to the procedure of Ref. [74], has the correct short and long-distance asymptotic behavior although the intershell bump is underestimated. An improved approximation that yields a more accurate intershell bump is also discussed in Ref. [74]. This approach is of practical interest since it is easier to construct self-interaction free, exchange-correlation functionals that depend on the orbitals instead of the density. Grabo and Gross [75] recently implemented this scheme with the approximation of Krieger, Li and Iafrate and the orbital-dependent correlation functional of Colle and Salvetti [76].

A different approximate scheme that cures the long-distance asymptotics of the exchange-correlation potential is obtained by combining a given approximate exchange-correlation functional with a self-interaction correction (SIC) procedure [19]. A GGA depending on the Laplacian of the density could be easily constructed so that the exchange-correlation potential does not have a spurious divergence at nuclei and could then be implemented in a SIC scheme to yield a potential with also the correct long-range asymptotic behavior.

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A. APPROXIMATE FUNCTIONAL FORMS OF $E_{\rm xc}\left[\rho\right]$

The second order generalized gradient approximation exchange-correlation energy is written as

$$E_{\rm xc}^{\rm GGA}\left[\rho\right] = \int d\mathbf{r}\, e_{\rm xc}(\rho(\mathbf{r}), \left|\nabla\rho(\mathbf{r})\right|, \nabla^2\rho(\mathbf{r})). \qquad (40)$$

We define the following density dependent variables:

$$k_{\rm F} = \left(3\pi^2\rho\right)^{1/3}, \quad k_s = \left(\frac{4}{\pi}k_{\rm F}\right)^{1/2}, \quad s = \frac{|\nabla\rho|}{2\,k_{\rm F}\,\rho}, \quad t = \frac{|\nabla\rho|}{2k_s\,\rho}, \quad r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}.$$

We present the spin unpolarized version of the approximate functionals, $\zeta = (\rho_\uparrow - \rho_\downarrow)/\rho = 0$. All the parameters that appear in the following functionals are in atomic units.

LDA exchange functional

$$e_{\mathrm{x}}^{\mathrm{LDA}} = A_x \rho^{4/3}\,, \tag{41}$$

where $A_{\mathrm{x}} = -(3/4)\,(3/\pi)^{1/3}$.

LDA correlation functional (Perdew-Wang [15])

$$e_{\mathrm{c}}^{\mathrm{LDA}} = -2a\rho\,(1+\alpha_1 r_s)\log\left[1+\frac{1}{2a(\beta_1 r_s^{1/2}+\beta_2 r_s+\beta_3 r_s^{3/2}+\beta_4 r_s^2)}\right]\,, \tag{42}$$

where $a = 0.0310907$, $\alpha_1 = 0.21370$, $\beta_1 = 7.5957$, $\beta_2 = 3.5876$, $\beta_3 = 1.6382$ and $\beta_4 = 0.49294$.

RPA correlation functional [77]

$$\begin{aligned} e_{\mathrm{c}} &= -\rho\, c^{\mathrm{P}} f(r_s/r^{\mathrm{P}}), \qquad (43)\\ f(z) &= (1+z^3)\ln\left(1+\frac{1}{z}\right)+\frac{z}{2}-z^2-\frac{1}{3}\,, \end{aligned}$$

where $c^{\mathrm{P}} = 0.0252$ and $r^{\mathrm{P}} = 30$.

Langreth-Mehl exchange-correlation functional [9]

$$e_{\mathrm{x}} = e_{\mathrm{x}}^{\mathrm{LDA}} - a\frac{|\nabla\rho|^2}{\rho^{4/3}}\left(\frac{7}{9}+18\,f^2\right)\,, \tag{44}$$

$$e_{\mathrm{c}} = e_{\mathrm{c}}^{\mathrm{RPA}}(\rho) + a\,\frac{|\nabla\rho|^2}{\rho^{4/3}}\left(2e^{-F}+18f^2\right)\,, \tag{45}$$

where $F = b\,|\nabla\rho|\,/\rho^{7/6}$, $b = (9\pi)^{1/6}\,f$, $a = \pi/(16(3\pi^2)^{4/3})$ and $f = 0.15$.

Perdew-Wang '86 exchange functional [12]

$$e_{\mathrm{x}} = e_{\mathrm{x}}^{\mathrm{LDA}}(\rho)\left(1+0.0864\,\frac{s^2}{m}+b\,s^4+c\,s^6\right)^m\,, \tag{46}$$

where $m = 1/15$, $b = 14$ and $c = 0.2$.

Perdew-Wang '86 correlation functional [13]

$$e_{\rm c} = e_{\rm c}^{\rm LDA}(\rho) + e^{-\Phi} C_{\rm c}(\rho) \frac{|\nabla\rho|^2}{\rho^{4/3}} \,, \tag{47}$$

where

$$\begin{aligned} \Phi &= 1.745\, \tilde{f}\, \frac{C_{\rm c}(\rho=\infty)}{C_{\rm c}(\rho)} \frac{|\nabla\rho|}{\rho^{7/6}} \,, \\ C_{\rm c}(\rho) &= C_1 + \frac{C_2 + C_3 r_s + C_4 r_s^2}{1 + C_5 r_s + C_6 r_s^2 + C_7 r_s^3} \end{aligned}$$

and $\tilde{f} = 0.11$, $C_1 = 0.001667$, $C_2 = 0.002568$, $C_3 = 0.023266$, $C_4 = 7.389 \cdot 10^{-6}$, $C_5 = 8.723$, $C_6 = 0.472$, $C_7 = 7.389 \cdot 10^{-2}$.

Perdew-Wang '91 exchange functional [14]

$$e_{\rm x} = e_{\rm x}^{\rm LDA}(\rho) \left[\frac{1 + a_1\, s \sinh^{-1}(a_2 s) + \left(a_3 + a_4 e^{-100\, s^2}\right)\, s^2}{1 + a_1\, s \sinh^{-1}(a_2 s) + a_5 s^4} \right] \,, \tag{48}$$

where $a_1 = 0.19645$, $a_2 = 7.7956$, $a_3 = 0.2743$, $a_4 = -0.1508$ and $a_5 = 0.004$.

Perdew-Wang '91 correlation functional [14]

$$e_{\rm c} = \left[e_{\rm c}^{LDA}(\rho) + \rho\, H(\rho, s, t) \right] \,, \tag{49}$$

where

$$\begin{aligned} H &= \frac{\beta^2}{2\alpha} \log\left[1 + \frac{2\alpha}{\beta} \frac{t^2 + A\, t^4}{1 + A\, t^2 + A^2 t^4}\right] + C_{\rm c0}\left[C_{\rm c}(\rho) - C_{\rm c1}\right] t^2 e^{-100\, s^2} \,, \\ A &= \frac{2\alpha}{\beta} \left[e^{-2\alpha \epsilon_{\rm c}^{\rm LDA}(\rho)/\beta^2} - 1 \right]^{-1} \end{aligned}$$

and $\alpha = 0.09$, $\beta = 0.0667263212$, $C_{c0} = 15.7559$, $C_{c1} = 0.003521$. The function $C_{\rm c}(\rho)$ is the same as for the Perdew-Wang '86 correlation functional. $\epsilon_{\rm c}^{\rm LDA}(\rho) = e_{\rm c}^{LDA}(\rho)/\rho$.

Becke '88 exchange functional [11]

$$e_{\rm x} = e_{\rm x}^{\rm LDA}(\rho) \left[1 - \frac{\beta}{2^{1/3} A_{\rm x}} \frac{x^2}{1 + 6\beta\, x \sinh^{-1}(x)} \right] \,, \tag{50}$$

where $x = 2\,(6\pi^2)^{1/3}\, s = 2^{1/3}\, |\nabla\, \rho|\, / \rho^{4/3}$, $A_{\rm x} = -(3/4)\,(3/\pi)^{1/3}$ and $\beta = 0.0042$.

Engel-Chevary-Macdonald-Vosko exchange functional [18]

$$e_{\mathrm{x}} = e_{\mathrm{x}}^{\mathrm{LDA}}(\rho)\frac{1 + a_1\xi + a_2\xi^2}{1 + b_1\xi + b_2\xi^2}\,, \tag{51}$$

where $\xi = s^2$ and $a_1 = 27.8428$, $a_2 = 11.7683$, $b_1 = 27.5026$ and $b_2 = 5.7728$.

Wilson-Levy correlation functional [16]

$$e_{\mathrm{c}} = \frac{a\,\rho + b\,|\nabla\rho|\,/\rho^{1/3}}{c + d\,|\nabla\rho|\,/(\rho/2)^{4/3} + r_s}\,, \tag{52}$$

where $a = -0.74860$, $b = 0.06001$, $c = 3.60073$ and $d = 0.90000$.

Closed shell Lee-Yang-Parr correlation functional [17]

$$e_{\mathrm{c}} = -a\frac{1}{1 + d\,\rho^{-1/3}}\left\{\rho + b\,\rho^{-2/3}\left[C_F\,\rho^{5/3} - 2t_W + \frac{1}{9}\left(t_W + \frac{1}{2}\nabla^2\rho\right)\right]e^{-c\,\rho^{-1/3}}\right\}\,, \tag{53}$$

where

$$t_W = \frac{1}{8}\left(\frac{|\nabla\rho|^2}{\rho} - \nabla^2\,\rho\right)$$

and $C_F = 3/10\,(3\pi^2)^{2/3}$, $a = 0.04918$, $b = 0.132$, $c = 0.2533$ and $d = 0.349$.

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