Accurate exchange-correlation potentials and total-energy components for the helium isoelectronic series

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Starting from very accurate many-body wave functions, we have constructed essentially exact densities, exchange-correlation potentials, and components of the total energy for helium and two-electron ions. These density-functional results are compared to the corresponding quantities obtained from a variety of commonly used approximate density functionals, namely, the local-density approximation and various generalized gradient approximations, in order to test the accuracy of the approximate functionals. Although the generalized gradient approximations yield improved energies compared to the local-density approximation, the exchange and correlation potentials (especially the latter) obtained from the generalized gradient approximations are in poor agreement with the corresponding exact potentials. The large-distance asymptotic behavior of the exact exchange-correlation potential to $\mathcal{O}(1/r^4)$ is found to agree with theoretical predictions. The short-range behavior of the exchange-correlation potential is very close to quadratic. The prospects for improved generalized gradient approximations are discussed.

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I. INTRODUCTION

Density-functional methods [1–3] are commonly used to study the electronic structure of both extended systems such as solids and solid surfaces and finite systems such as atoms and molecules. Until recently, the vast majority of density-functional calculations have employed the local-density approximation(LDA) for the exchange and correlation energy [2]. Whereas the local-density approximation has been remarkably successful given its simplicity, it has well-documented limitations, such as its tendency to yield binding energies of molecules and solids that are too large and bond lengths of weakly interacting systems that are too small. In the last decade a large number of generalized-gradient-approximation (GGA) functionals have been proposed [4–12] that employ not only the local value of the density, but also its derivatives in the expression for the exchange-correlation energy functional. There exists a rapidly growing body of literature on applying these functionals to calculate various properties of atoms, molecules, and solids. Whereas it is necessary and useful to build a body of information concerning which properties of which materials are treated more accurately or less accurately in GGA relative to LDA, it is unsatisfactory that, at the present time, there is very little understanding of why the various GGAs, in the various applications, do or do not succeed in improving upon LDA. Also, the number of proposed GGA functionals is large and growing and it is both very time consuming and not particularly enlightening to test each of them in a large number of calculations. Furthermore, the presence of various other approximations in the calculations sometimes results in significantly different results when the same material is calculated with the same functional using different computational schemes. It is the purpose of this paper to test the various approximate functionals for a set of systems for which the exact density-functional quantities can be calculated. The commonly used functionals have been constructed to accurately reproduce the exchange-correlation energy, which is an integrated quantity. Instead, we study not only the exchange-correlation energy, but also the exchange-correlation energy density and potential, which contain far more detailed information. We note that whereas the exchange-correlation energy density is not uniquely defined, the exchange-correlation potential is, making the latter the more important quantity in our study.

In this paper we obtain essentially exact density-functional quantities for the helium isoelectronic sequence and use these to assess the adequacy of the LDA and the various GGAs. There are several earlier papers [13–16] that have also used helium and two-electron ions as test cases, but all of them have lacked sufficient accuracy to observe the correct short-distance or long-distance behavior of the exchange-correlation potential, both of which are very sensitive to fine details of the charge density.

Of the several LDA parametrizations that have been proposed over the years, the two that are presently accepted as being accurate [17,18] are in rather close agreement with each other since they are both fitted to the

same Green's function Monte Carlo [19] data and are constrained to reduce to the known high-density expression [20]. On the other hand, the commonly used GGAs [4–9] are significantly different from each other. In this paper we have systematically tested all the proposed GGAs (that have received any appreciable measure of use in electronic structure calculations and that have not been superseded by more recent versions due to the same authors) on the exact (non-self-consistent) densities. In addition, we have tested the recent Perdew-Wang 1991 functional [6] in self-consistent calculations. We select this particular GGA because (a) it is a recent improvement to an earlier GGA [5], both of which have received considerable attention, and (b) it satisfies a large number of the known properties of the exact density functional (see Table IV of Ref. [21]).

The layout of this paper is as follows. In Sec. II we describe the form of the very accurate wave functions. In Sec. III we describe the calculation of the density from the wave functions and compare the almost exact density with that obtained from the LDA, from the Perdew-Wang 1991 GGA, and from the Hartree-Fock approximation. In Sec. IV we evaluate accurate exchange-correlation potentials for five members of the helium isoelectronic series and discuss the short-distance and long-distance asymptotic behavior, both of which are very sensitive to fine details in the density. In Sec. V we compare the accurate exchange and correlation potentials, energy densities, and energies with those obtained from approximate functionals, evaluated for the exact (non-self-consistent) density for helium. In Sec. VI we compare the accurate exchange-correlation potentials and components of the total energy to those obtained self-consistently from (a) the local-density approximation, (b) the Perdew-Wang 1991 generalized gradient approximation, and (c) the Hartree-Fock approximation. Finally, in Sec. VII we discuss various features of the existing GGAs and the possibility of constructing a more accurate GGA by including terms containing the Laplacian of the density.

II. WAVE FUNCTIONS

It is necessary to employ very accurate wave functions in order to observe the true short-distance and long-distance behavior to $O(1/r)$ of the exchange-correlation potential. The form of the wave function used is that of Ref. [22]. The criteria for the selection of terms in the wave function are those of Ref. [23] and are motivated by the analytic structure of the Fock expansion [24]. The wave functions of S states of the helium isoelectronic sequence can be written in terms of three independent coordinates, which may be chosen to be the interparticle distances r_1, r_2, r_{12} or equivalently the Hylleraas coordinates

$$s = r_1 + r_2, \quad t = r_1 - r_2, \quad u = r_{12}. \tag{1}$$

The wave functions are expanded in the basis functions $\phi_{n,l,m,j}(2Zks, 2Zkt, 2Zku)$, where Z is the nuclear charge, k is a scale factor, and

$$\phi_{n,l,m,j}(s,t,u) = s^n t^l u^m (\ln s)^j e^{(-s/2)}, \tag{2}$$

where the integers n, l, m, j obey the constraints

$$0 \le l, \quad 0 \le m, \quad 0 \le 2j \le n + l + m \tag{3}$$

and negative values of n are permitted only if $2j + 2 \le n + l + m$. These restrictions [23] follow from the analytic structure of the Fock expansion [24]. Antisymmetry of the wave functions implies that for singlet states l must be even and for the triplet states it must be odd. The values of the scale factor k used are those of Ref. [23], $k = 0.39, 0.8, 0.96, 1.0$, and 1.0 for H^-, He, Be^{2+}, Ne^{8+}, and Hg^{78+}, respectively.

Most of the calculations were performed with a 491-term wave function, corresponding to $(n + l + m)_{\max} = 6$ and $(l + m)_{\max} = 12$. The accuracy of the results was checked by employing smaller bases with 166 terms corresponding to $(n+l+m)_{\max} = 4$ and $(l+m)_{\max} = 10$ and 286 terms corresponding to $(n + l + m)_{\max} = 5$ and $(l + m)_{\max} = 11$ [25]. The relative error in the energy for a fixed basis size goes down with increasing Z. The difference in energy between the 166-term and the 491-term wave functions is 1 part in 10^7 for H^-, 2 parts in 10^{11} for He, and 3 parts in 10^{15} for Hg^{78+}. The difference in energy between the 286-term and the 491-term wave functions is 1 part in 10^9 for H^-, 7 parts in 10^{15} for He, and 1 part in 10^{17} for Hg^{78+}. The energy of the 491-term wave function is estimated to be better than 3 parts in 10^{11} for H^-, 1 part in 10^{16} for He, and 1 part in 10^{19} for Hg^{78+}. In order to achieve this high accuracy, the calculations of the wave functions were performed using 128-bit (quadruple-precision) arithmetic. In the case of H^-, where one of the two electrons has a high probability of being far from the nucleus, yet a better rate of convergence can be obtained by including additional basis functions that are well suited to describe the in-out correlation of the two electrons, as were employed by Frankowski [26] and Baker, Hill, and Morgan [27] in the study of excited states.

III. DENSITIES

The charge density is

$$\rho(\mathbf{r}_1) = 2\pi \int_0^\infty dr_2\, r_2^2 \int_0^\pi d\theta_2\, \sin\theta_2\, \psi^2(\mathbf{r}_1, \mathbf{r}_2). \tag{4}$$

If the integrals are performed using a Newton-Cotes integration formula (e.g., Bode integration), then the integral converges rather slowly owing to presence of the electron-electron cusp in the integrand. A more rapid convergence of the integrals can be obtained by instead evaluating the charge density as

$$\rho(\mathbf{r}_1) = \tilde{\rho}(\mathbf{r}_1) - I\psi^2(\mathbf{r}_1, \mathbf{r}_1), \tag{5}$$

where

$$\tilde{\rho}(\mathbf{r}_1) = 2\pi \int dr_2\, r_2^2 \int d\theta_2\, \sin\theta_2\, [\psi^2(\mathbf{r}_1, \mathbf{r}_2) + \psi^2(\mathbf{r}_1, \mathbf{r}_1) \times e^{-\{r_{12} + \frac{(Zr_{12})^2}{8}\}}],$$
$$I = 4\pi \int dr_{12}\, r_{12}^2\, e^{-\{r_{12} + \frac{(Zr_{12})^2}{8}\}}. \tag{6}$$

The first term in the exponent removes the cusp in the square of the wave function while the second term ensures that the function that is added in decays more rapidly than $\psi^2(\mathbf{r}_1,\mathbf{r}_2)$ for large r_{12}. With this change, the rate of convergence of the integrals, performed by Bode integration, is $1/n^6$, where n is the number of points in each coordinate direction. This method was successfully implemented, but it was found that it is more efficient to use instead an adaptive Gauss-Legendre method to perform the integrals in Eq. (4), which introduces additional integration points as needed to achieve the desired accuracy. The results presented here used the latter method.

In Fig. 1 the self-consistent densities obtained from LDA, the Perdew-Wang 1991 GGA [6], and the Hartree-Fock approximation are compared to the accurate density. The LDA density is less peaked than the true density, while the Hartree-Fock density is very close to and slightly more peaked than the true density. Figure 2 shows the error in the LDA, GGA, and Hartree-Fock densities. Note that the Hartree-Fock density is considerably more accurate than the LDA and the GGA density.

IV. ACCURATE EXCHANGE-CORRELATION POTENTIALS AND ENERGIES

The total ground-state energy of a system of N interacting electrons in an external potential v_{ext} is given in the Kohn-Sham formulation [1,2] of density-functional theory by the expression (we use atomic units $\hbar = e = m = 1$ throughout)

$$E = -\frac{1}{2}\sum_{i=1}^{N}\int \psi_i \nabla^2 \psi_i \, d\mathbf{r} + \int \rho(\mathbf{r})\, v_{\text{ext}}(\mathbf{r})\, d\mathbf{r} + \frac{1}{2}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}' + E_{\text{xc}}[\rho], \quad (7)$$

where

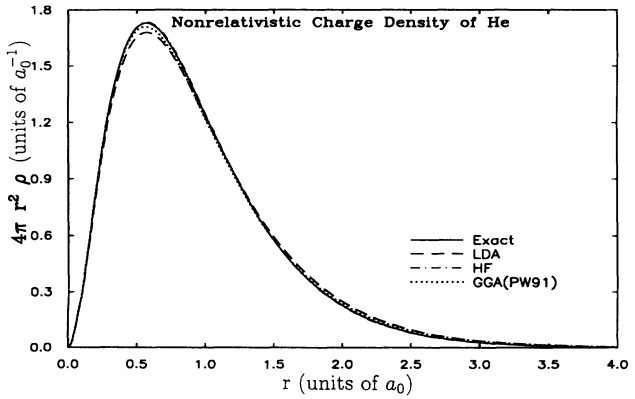

FIG. 1. Comparison of the LDA, the GGA (Perdew-Wang 1991), the Hartree-Fock approximation, and exact densities of He. The difference between the Hartree-Fock and exact curves is barely discernible.

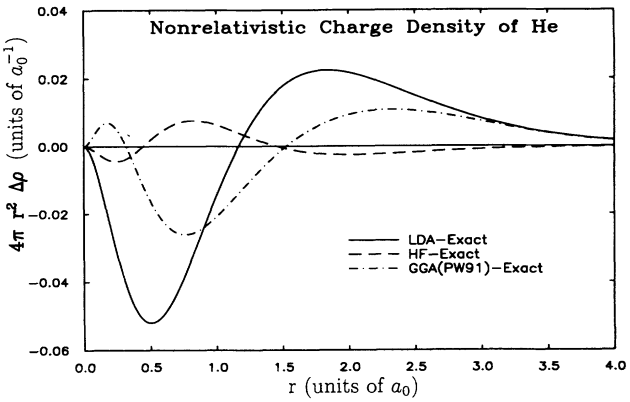

FIG. 2. Errors in the LDA, the GGA, and the Hartree-Fock densities of He.

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 . \quad (8)$$

The single-particle orbitals $\psi(\mathbf{r})$ are solutions of the equation

$$\left\{-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}([\rho];\mathbf{r})\right\}\psi_i = \epsilon_i \psi_i, \quad (9)$$

where $v_{\text{xc}}([\rho];\mathbf{r})$ is the functional derivative of the exchange-correlation energy functional $E_{\text{xc}}[\rho]$.

Given the exact density of some arbitrary many-electron system, it is possible to determine the exact density functional $v_{\text{xc}}(\mathbf{r})$. In general, the exact $v_{\text{xc}}(\mathbf{r})$ can be determined by expanding $v_{\text{xc}}(\mathbf{r})$ in a complete set of basis functions and varying the expansion coefficients such that Eqs. (9) and (8) yield the exact density [28]. If the exact energy E is also known, then the exact E_{xc} can be obtained from Eq. (7).

In the special case of the singlet ground state of a two-electron system a simpler procedure suffices because the single occupied orbital is simply related to the electronic density

$$\psi(\mathbf{r}) = \left[\frac{\rho(\mathbf{r})}{2}\right]^{1/2} \quad (10)$$

and the eigenvalue is given by $\epsilon = E + Z^2/2$. The latter relation follows from the fact that the highest occupied Kohn-Sham eigenvalue of a many-body system equals the ionization energy [29]. The total energy E is obtained variationally using the wave functions described in Sec. II. Hence v_{xc} can be obtained by inverting the single-particle Kohn-Sham equation

$$v_{\text{xc}}([\rho];\mathbf{r}) = \epsilon_{\text{KS}} + \frac{1}{2}\frac{\nabla^2\psi}{\psi} - v_{\text{ext}}(\mathbf{r}) - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \quad (11)$$

The exchange energy for two-electron systems can be written directly in terms of the density

$$E_x[\rho] = -\frac{1}{4}\int\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}' \tag{12}$$

$$= \int \rho(\mathbf{r})\epsilon_x(\mathbf{r})\,d\mathbf{r}, \tag{13}$$

where

$$\epsilon_x(\mathbf{r}) = -\frac{1}{4}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}' \tag{14}$$

is the exchange energy density per electron. Note that one could consider a definition of exchange energy in term of the Hartree-Fock density instead of the exact density. In Sec. VI we will compare these two slightly different definitions.

$v_x([\rho];\mathbf{r})$ is the functional derivative of E_x with respect to the density, which gives

$$v_x([\rho];\mathbf{r}) = -\frac{1}{2}\int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'. \tag{15}$$

It cancels the self-interaction term in the Hartree potential. The correlation energy and potential are obtained by taking the difference

$$E_c[\rho] = E_{xc}[\rho] - E_x[\rho] \tag{16}$$

and

$$v_c([\rho];\mathbf{r}) = v_{xc}([\rho];\mathbf{r}) - v_x([\rho];\mathbf{r}). \tag{17}$$

A. Comparison of the exact v_x and v_c for the isoelectronic sequence

Approximate trial wave functions of the form $\psi = e_xp[-\zeta(r_1+r_2)]$ have a minimum in the expectation value of the energy for $\zeta = Z - 5/16$. The Hartree potential at the origin resulting from the density corresponding to this wave function is $2(Z-5/16)$. Motivated by this, in Fig. 3 we plot the exact $v_x/(Z-5/16)$ obtained from Eq. (15) versus $(Z-5/16)r$ for the helium isoelectronic sequence. The curves for different Z nearly lie on a single universal curve; only H^- deviates appreciably from it. The inset is a plot of v_x/Z versus Zr.

Figure 4 is a plot of v_c versus Zr. In contrast to other quantities of interest, the magnitude of v_c gets smaller with increasing Z. This is clearly different from the LDA v_c, which must get deeper with increasing ρ and consequently increasing Z. Since the external potential, at a given value of Zr, scales as Z^2, an accurate evaluation of v_c for large Z requires calculations of progressively higher accuracy.

B. Short-distance behavior of v_x and v_c

Since the exchange potential v_x for a two-electron system in its ground state is just minus half the Hartree potential, it is apparent that v_x must be quadratic at the nucleus. However, from Fig. 9 it is apparent that even v_c is nearly quadratic at the nucleus, though we know of no theoretical reason why this must be rigorously true. Earlier evaluations of v_c lacked sufficient accuracy to observe this nearly quadratic behavior. In fact, some earlier work found a spurious divergence [14,15] in v_{xc} because of the failure of the density to satisfy the cusp condition [30,31] at the nucleus. Other papers [13,16] found that v_{xc} is finite at the nucleus, but failed to observe the nearly quadratic behavior. For a two-electron system it follows from Eq. (11) that near the nucleus

$$v_{xc}(\mathbf{r}) = \epsilon - v_H(0) + \frac{3}{2}\frac{\psi''}{\psi} - Z^2 + \left(\frac{\psi'''}{\psi} + 2Z\frac{\psi''}{\psi} - Z^3\right)r + O(r^2) \tag{18}$$

or equivalently, using Eq. (10),

$$v_{xc}(\mathbf{r}) = \epsilon - v_H(0) + \frac{3}{4}\frac{\rho''}{\rho} - \frac{5}{2}Z^2 + \left(\frac{\rho'''}{2\rho} + \frac{5Z}{2}\frac{\rho''}{\rho} - 6Z^3\right)r + O(r^2), \tag{19}$$

where the primes denote derivatives with respect to r. For all the two-electron systems studied here, the coefficient of the linear term in r is close to zero.

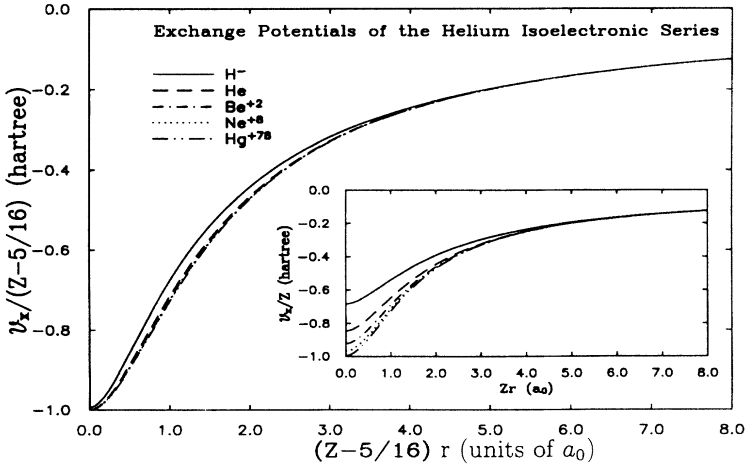

FIG. 3. Exchange potentials for the He isoelectronic sequence.

Although we do not have a proof that the true density functional v_c must be quadratic at nuclei, it is worth noting that the Harbola-Sahni potential [32], which is related to (at least for exchange) but different from the true density-functional potential [33], is quadratic. The Harbola-Sahni potential is the work done by the electron in the field of its (dynamically changing) exchange-correlation hole as it moves from infinity to the position of interest. By symmetry, the exchange-correlation hole must be spherical when the electron is at the nucleus. Also, when the electron is close to the nucleus, the displacement of the center of the exchange-correlation hole from the electron is linear in the distance of the electron from the nucleus. Hence the field acting on the electron is linear in its displacement from the nucleus and the potential is quadratic.

C. Long-distance behavior of v_x and v_c

Since $v_x = -v_H/2$, it is clear that at large distances $v_x \sim -1/r$ plus exponentially small terms, since the density decays exponentially. It has been shown in Ref. [29] that, in the case of an n electron atom or ion with orbitally nondegenerate n and $n-1$ electron ground states, $v_c \sim -\alpha/2r^4$, as $r \to \infty$, where α is the dipole polarizability of the $n-1$ electron system. In the case of the two-electron systems treated here, the dipole polarizability of the residual one-electron system is $\alpha = 9/(2Z^4)$. Due to the rapid $1/r^4$ falloff, this asymptotic behavior is not discernible in a plot of v_c versus r such as Fig. 4. In Fig. 5 we plot $r^4 v_c$ for H^-, which converges to -9/4 at large r as expected. Note that v_c becomes negative and approaches its asymptotic behavior only at very large r, in a region that contributes very little to the total energy. It is possible to see this asymptotic behavior only because we have used very accurate wave functions to construct the density. All earlier papers [13–16] lacked sufficient accuracy to observe this asymptotic behavior or even that v_c is negative at large distances.

Since in the asymptotic region the electron is well separated from the rest of the system, classical arguments

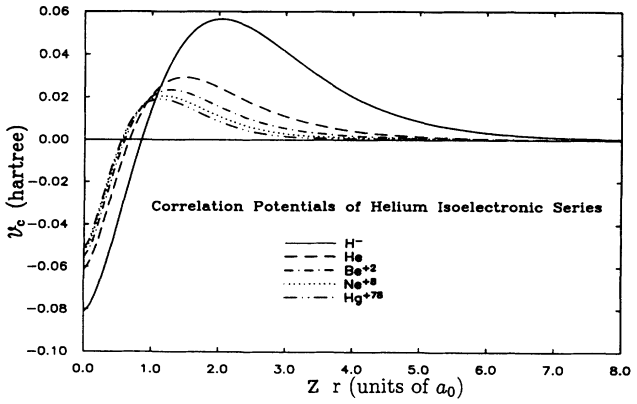

FIG. 4. Correlation potentials for the He isoelectronic sequence.

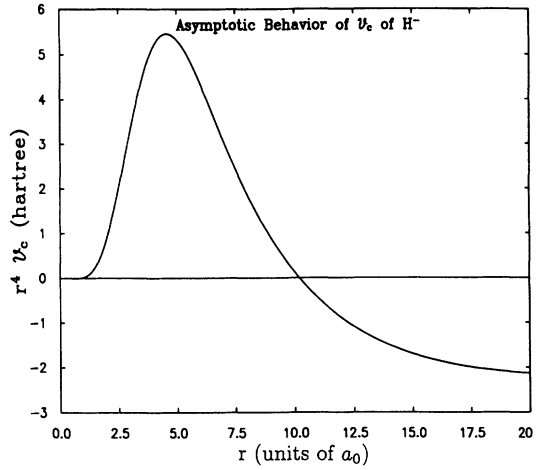

FIG. 5. Asymptotic behavior of the correlation potential v_c of H^-.

can be used to deduce v_c. It is then clear that v_c will have contributions from all even negative powers of r, smaller than or equal to -4. Hence the next higher-order term will be $O(1/r^6)$, which will contain contributions from both the quadrupole induced by the gradient of the electric field and the octupole induced by the electric field. In addition, v_c will contain an exponentially decaying contribution arising from the fact the potential is not due to pointlike multipoles, but an exponentially decaying density. A plot of $\ln(v_c + \alpha/2r^4)$ versus r shows that even at the largest distances shown in Fig. 5, the $O(1/r^6)$ term is smaller than the exponential term, though of course at sufficiently large distances the $O(1/r^6)$ term must dominate. The exponent is the same as that of $v_x + 1/r$, since both exponents arise from the exponential decay of the density.

It is worth noting that v_c is sensitive to the details of the problem. Although v_c has qualitatively the same behavior for the two-electron atom and ions (i.e., it is negative at small r, positive at intermediate r, and negative at large r), it has qualitatively the opposite behavior for closely related systems consisting of two electrons in harmonic potentials [34].

V. COMPARISON OF EXACT AND APPROXIMATE QUANTITIES FOR THE EXACT DENSITY OF HELIUM

A. Comparison of $\epsilon_x, \epsilon_c, v_x$, and v_c

The various GGAs express the exchange-correlation energy as

$$E_{xc}^{GGA}[\rho] = \int e_{xc}\left(\rho, |\nabla\rho|, \nabla^2\rho\right) d\mathbf{r}. \tag{20}$$

In Fig. 6 we compare the LDA and various GGA exchange energy densities per electron $\epsilon_x = e_x/\rho$ from Eq. (20) with the exact exchange energy density per electron from Eq.(14). The definition of the exchange energy

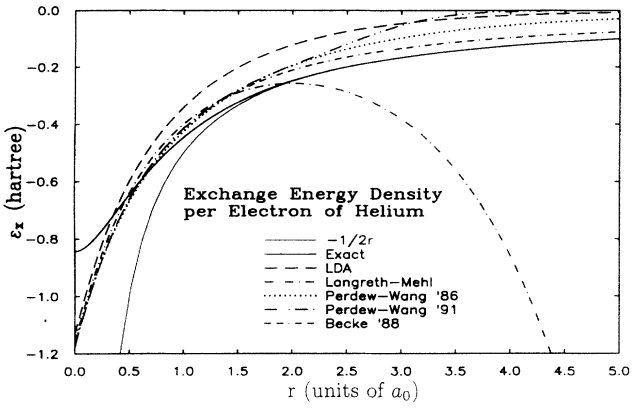

FIG. 6. Comparison of the exact and the various approximate exchange energy densities per electron. Both the exact and the approximate energies are evaluated for the exact density of He.

density is not unique, but a natural definition, which follows from writing the Hartree-Fock exchange energy in terms of the first-order density matrix, results in an ϵ_x that at large distances goes as $-1/2r$ [35]. In the case of ground states of two-electron systems, this definition reduces to Eq. (14). At large r, the approximate ϵ_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 $-1/2r$ for exponentially decaying densities. However, as also noted by Engel *et al.* [10], the Becke ϵ_x achieves its asymptotic behavior at much larger distances than does the true ϵ_x. This is because the correction to the leading $-1/r$ term is exponentially small for the true functional but $O(1/r^2)$ for the Becke functional. Note also that the Becke ϵ_x has a wrong asymptotic behavior $-1/r$ for densities that have a Gaussian decay [34].

In Fig. 7 we compare the LDA and various GGA correlation energy densities, $\epsilon_c = e_c/\rho$. They differ greatly from each other.

We note that the exchange-correlation energy density is not uniquely defined, but the integrated quantity E_{xc} and the functional derivative v_{xc} are unique. Accordingly the differences of approximate energy densities from each other and from the "true" exchange energy density are not necessarily indicative of a failure of the approximate functionals. It is v_{xc} that controls the self-consistent charge density; accordingly we study v_x and v_c next.

The exchange-correlation potential is the functional derivative of Eq.(20)

$$v_{xc}([\rho];\mathbf{r}) = \left[\frac{\partial e_{xc}}{\partial \rho} - \nabla\cdot\left(\frac{\partial e_{xc}}{\partial \nabla\rho}\right) + \nabla^2\left(\frac{\partial e_{xc}}{\partial \nabla^2\rho}\right)\right]_{\rho(\mathbf{r}),\nabla\rho(\mathbf{r}),\nabla^2\rho(\mathbf{r})} \quad (21)$$

In Fig. 8 we compare v_x obtained from LDA and the various GGAs evaluated for the exact charge density with the exact v_x obtained from Eq. (15). The approximate potentials differ significantly from the exact potential. 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 [7], which behaves as $(-\text{const}/r^2)$ [10], and the Langreth-Mehl functional, which diverges [4]. The Perdew-Wang 1991 functional has a spurious minimum between $2.5a_0$ and $3.5\ a_0$. It also has spurious oscillations near quadratic extrema of the charge density [34]. This is due to the fact that the effective coefficient of the $|\nabla\rho|^2$ term increases very rapidly from the known value specified by the second-order gradient expansion at $\xi = 0$ to a value that is 2.1 times as large at $\xi = 0.04$, where $\xi = [\nabla\rho/(2k_F\rho)]^2$ and k_F is the Fermi wave vector, as can be seen in Fig. 2 of Ref. [36].

At the origin, the exact exchange potential has a quadratic minimum because it is simply proportional to the negative of 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 the LDA potential,

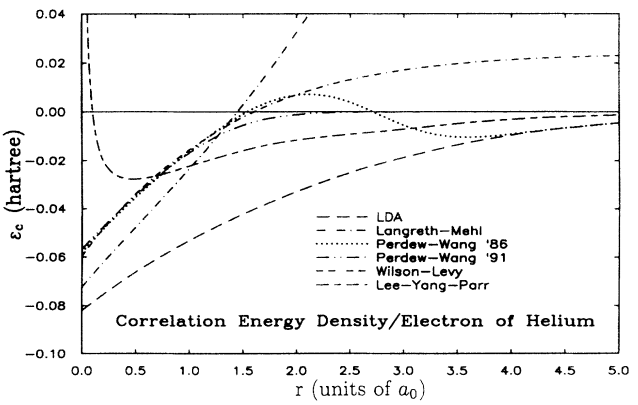

FIG. 7. Comparison of the various approximate correlation energy densities per electron. The approximate energies are evaluated for the exact density of He.

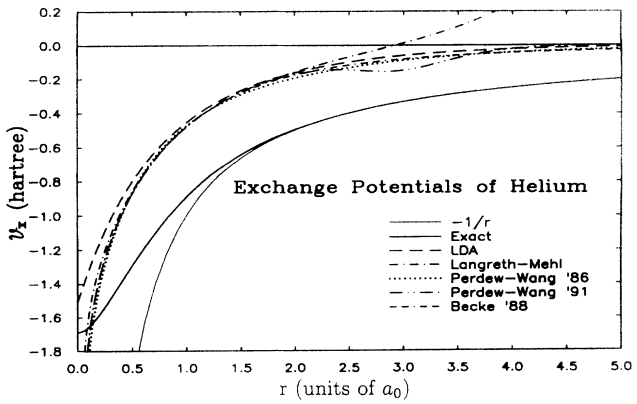

FIG. 8. Comparison of the exact and the various approximate exchange potentials. Both the exact and the approximate potentials are evaluated for the exact density of He.

but the more negative values of the GGA potentials at short and intermediate distances is a step in the right direction.

In fact it is possible to show that any GGA that has terms containing $\nabla\rho$, but no higher derivatives of ρ *must* yield a v_{xc} that diverges at nuclei. If $\rho \sim \text{const}+r^s$ 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

$$\frac{\partial e_{xc}}{\partial \nabla\rho} \sim |\nabla\rho|^{m-1} \sim r^{(s-1)(m-1)} \tag{22}$$

and

$$\nabla \cdot \left(\frac{\partial e_{xc}}{\partial \nabla\rho}\right) \sim r^{(s-1)(m-1)-1}. \tag{23}$$

Hence the exchange-correlation potential diverges at the origin when

$$(s-1)(m-1)-1 < 0, \tag{24}$$

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 [8] and for all values of m if $s \leq 1$. At nuclei, $s = 1$ and v_{xc} always diverges. The divergence for atoms can be eliminated by including appropriate terms containing $\nabla^2\rho$ [37].

Pedroza [15] observed the divergence of the Langreth-Mehl v_{xc}, but since his "exact" v_{xc} also had a spurious divergence, he viewed the divergence of the Langreth-Mehl v_{xc} in a positive light.

In Fig. 9 we compare approximate correlation potentials of He, obtained from Eq. (21), to the exact correlation potential obtained from Eq. (17). At large r, the approximate potentials go to zero exponentially with the exception of the Wilson-Levy potential [8], which goes to a positive constant, and the Langreth-Mehl functional, which diverges. All of the GGA correlation potentials diverge at the origin. It follows from Eq. (24) that this must be the case for all the GGAs which do not contain derivatives higher than first order. Of the GGAs proposed so far, only the Lee-Yang-Parr GGA contains Laplacian terms, but not in the form necessary to eliminate the divergence in the correlation potential.

B. Comparison of E_x, E_c, and E_{xc}

Table I shows the nonrelativistic total energy and its components for five members of the helium isoelectronic series. The total energies given are those for the 491-term wave function. The kinetic contribution to E_c can be obtained as the difference of the true many-body kinetic energy (which equals the negative of the total energy, by the virial theorem) and the true Kohn-Sham single-particle kinetic energy. It ranges from 0.027 882 hartree for H^- to 0.046 403 hartree for Hg^{78+}. From Table I we see that the heavier systems approximately satisfy the simple form of the virial theorem, which is that the kinetic contribution to E_c is $-E_c$. In fact this simple form has been shown to apply in the high-density limit [38,39]. This result follows from the general form of the virial theorem for correlation [40] and the work in Ref. [41].

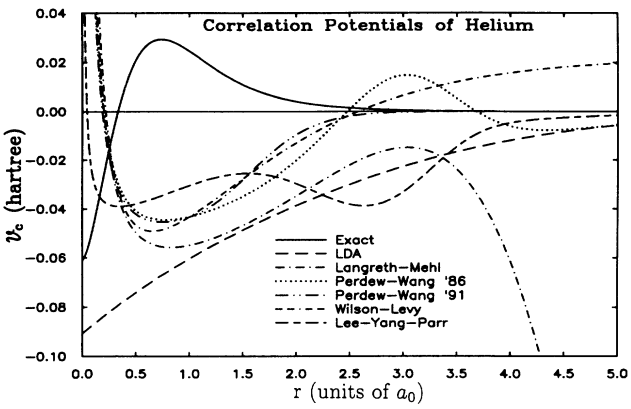

FIG. 9. Comparison of the exact and the various approximate correlation potentials. Both the exact and the approximate potentials are evaluated for the exact density of He.

For the heavier systems there appears to be an approximate virial theorem, i.e., the kinetic contribution to E_c is approximately $-E_c$. In fact such a theorem has been proven in the high-density limit by Perdew [38] and Gorling *et al.* [39].

In Table II we compare the approximate E_x, E_c, and E_{xc} evaluated for the exact density with the corresponding exact quantities. As is well known, LDA yields values of E_x that are too small in absolute magnitude and values of E_c that are too large in absolute magnitude, resulting in a cancellation of errors for E_{xc}. With the exception of the Langreth-Mehl correlation energy for the heavier ions, all the GGAs yield improved energies compared to LDA. The correlation energies are nearly independent of the nuclear charge Z and the exact exchange energies scale approximately linearly with $Z - 5/16$. This former behavior is not universal; e.g., for the Be isoelectronic sequence E_c scales approximately linearly with Z.

The conventional quantum chemistry definition of E_x

TABLE I. The nonrelativistic total energy and its components for the helium isoelectronic series. All energies are in hartrees and are accurate to all digits quoted.

Ion	E_{tot}	E^s_{kin}	E_{en}	E_H	E_{xc}
H^-	-0.527 751 016 5	0.499 869	-1.366 524	0.761 796	-0.422 892
He	-2.903 724 377 034 118	2.867 082	-6.753 267	2.049 137	-1.066 676
Be^{2+}	-13.655 566 238 423 582	13.614 084	-29.502 003	4.553 255	-2.320 902
Ne^{8+}	-93.906 806 515 037 541	93.862 251	-193.750 849	12.054 968	-6.073 176
Hg^{78+}	-6350.157 557 832 474 797	6350.111 155	-12 750.000 108	99.555 863	-49.824 467

TABLE II. Comparison of exchange and correlation energies of the helium isoelectronic series for LDA and the various GGAs with those for the exact density functional. The approximate functionals are evaluated for the exact (not the self-consistent) densities. The numbers in parentheses are the percentage errors.

Functional	Ion	Exact	LDA (Perdew-Wang)	Langreth-Mehl	Perdew-Wang 1986	Perdew-Wang 1991	Becke 1988	Wilson-Levy	Lee-Yang-Parr
E_x	H^-	-0.380 898	-0.337 (12%)	-0.387 (-2%)	-0.400 (-5%)	-0.393 (-3%)	-0.395 (-4%)		
	He	-1.024 568	-0.883 (14%)	-1.014 (1%)	-1.033 (-1%)	-1.016 (1%)	-1.025 (-0%)		
	Be^{2+}	-2.276 628	-1.957 (14%)	-2.246 (1%)	-2.279 (-0%)	-2.245 (1%)	-2.265 (1%)		
	Ne^{8+}	-6.027 484	-5.173 (14%)	-5.940 (1%)	-6.015 (0%)	-5.927 (2%)	-5.982 (1%)		
	Hg^{78+}	-49.777 931	-42.699 (14%)	-49.036 (1%)	-49.605 (0%)	-48.889 (2%)	-49.348 (1%)		
E_c	H^-	-0.041 995	-0.072 (-71%)	-0.049 (-16%)	-0.038 (10%)	-0.032 (24%)		-0.032 (25%)	-0.030 (29%)
	He	-0.042 107	-0.112 (-167%)	-0.050 (-19%)	-0.044 (-4%)	-0.046 (-9%)		-0.042 (1%)	-0.044 (-4%)
	Be^{2+}	-0.044 274	-0.150 (-240%)	-0.025 (43%)	-0.049 (-12%)	-0.053 (-21%)		-0.045 (-2%)	-0.049 (-10%)
	Ne^{8+}	-0.045 692	-0.202 (-342%)	0.082 (279%)	-0.084 (-83%)	-0.062 (-35%)		-0.047 (-3%)	-0.050 (-9%)
	Hg^{78+}	-0.046 536	-0.326 (-600%)	1.833 (4038%)	-0.299 (-543%)	-0.081 (-73%)		-0.048 (-3%)	-0.050 (-8%)
E_{xc}	H^-	-0.422 893	-0.408 (3%)	-0.435 (-3%)	-0.438 (-4%)	-0.425 (-0%)			
	He	-1.066 676	-0.996 (7%)	-1.064 (0%)	-1.077 (-1%)	-1.062 (0%)			
	Be^{2+}	-2.320 902	-2.107 (9%)	-2.271 (2%)	-2.328 (-0%)	-2.298 (1%)			
	Ne^{8+}	-6.073 176	-5.375 (11%)	-5.858 (4%)	-6.099 (-0%)	-5.989 (1%)			
	Hg^{78+}	-49.824 467	-43.025 (14%)	-47.203 (5%)	-49.904 (-0%)	-48.970 (2%)			

is that it is the exchange energy in a Hartree-Fock calculation. We prefer instead to define E_x and E_c in terms of the true density rather than the Hartree-Fock density. The difference is minor; for He, E_x using ρ_{HF} is $-1.025\,769$ hartree, whereas E_x using ρ is -1.024 568 hartree.

VI. COMPARISON OF EXACT AND APPROXIMATE QUANTITIES FOR THE SELF-CONSISTENT DENSITY OF He

A. Comparison of v_x and v_c

The approximate functionals in the preceding section were evaluated for the exact density. Here we study the effects of self-consistency. In Fig. 10 we compare the self-consistent LDA and the Perdew-Wang 1991 exchange-correlation potentials, for helium, to the exact one. Since the change in the exchange-correlation potentials for the approximate functionals is small compared to the difference between the exact and approximate functionals, we do not present results for the complete set of functionals studied in the preceding section. In Fig. 10 we also present the exact v_x evaluated from Eq. (15), which is very close to the self-consistent Hartree-Fock exchange potential (which is a local potential for helium). Since the electrons in Hartree-Fock theory do not interact with themselves, the Hartree-Fock potential has the correct long-distance $-1/r$ behavior, whereas the LDA and the Perdew-Wang 1991 potentials do not.

In Fig. 11 we compare the self-consistent LDA and the Perdew-Wang 1991 correlation potentials, for helium, to the exact one computed from Eq. (17). The solid line is obtained using the true charge density in constructing v_x while the dotted line is obtained by constructing v_x from the Hartree-Fock density. They are very close to each other. Amusingly, the Perdew-Wang 1991 potentials would bear a closer resemblance to the true potential if the sign were reversed.

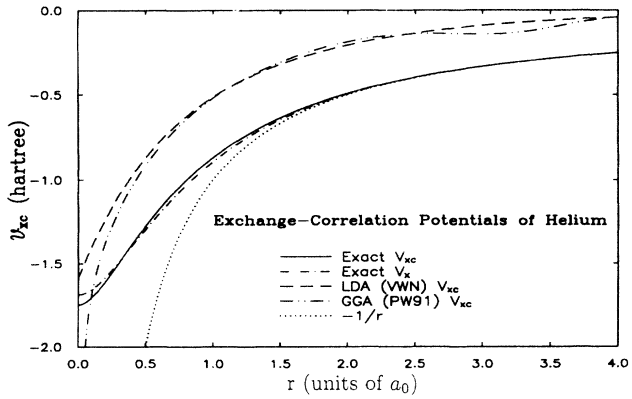

FIG. 10. Comparison of the LDA, the Perdew-Wang 1991 exchange-correlation potentials, and the exact exchange-correlation potential. The approximate potentials are evaluated for the self-consistent densities.

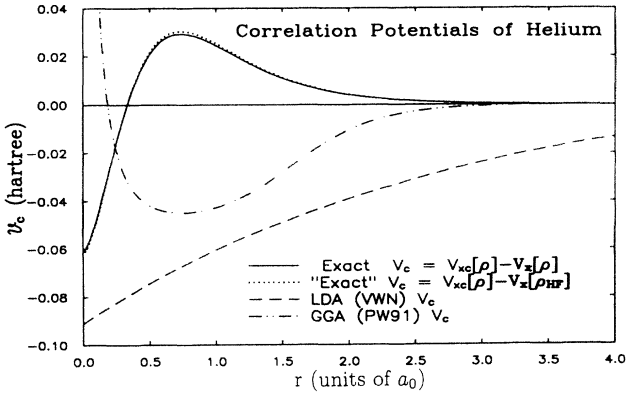

FIG. 11. Comparison of the LDA, the Perdew-Wang 1991 correlation potentials, and the exact correlation potential. The approximate potentials are evaluated for the self-consistent densities.

B. Comparison of components of the total-energy and single-particle eigenvalues

In Table III we compare the self-consistent total energy and its components, the density weighted expectation value of the exchange-correlation potential, and the single-particle eigenvalue from the LDA and the Perdew-Wang 1991 GGA to the corresponding exact values. Although the differences between the approximate and exact densities in Fig. 1 appear small visually, the effect of self-consistency upon the energy components is not completely negligible. The values of E_{en} and E_H depend solely on the charge density, and so their errors, given in the last two columns of Table III, reflect the difference between the true charge density and the self-consistent charge densities. Comparing the values in Tables II and III we observe that the LDA and the Perdew-Wang 1991 GGA values of E_{xc} for He are in error by 0.071 and 0.005 H, respectively, when evaluated for the exact density, but by 0.093 and 0.012 hartree, respectively, when evaluated for the self-consistent densities.

In contrast to the potential, the values of the total-energy and total-energy components are much improved by the Perdew-Wang 1991 GGA relative to the LDA. On the other hand, the single-particle eigenvalue is not appreciably improved, since v_{xc} is not much different for this GGA and LDA, except close to the nucleus. Though not shown in Table III, we have verified that the Perdew-Wang 1991 GGA yields improved total energies and total-energy components for self-consistent calculations of Be^{2+}, Ne^{8+}, and Hg^{78+} also. (It is not possible to perform a self-consistent calculation of H^- with either functional without immersing the ion in an external potential to localize the second electron.)

Note that in Table III all the components of the total energy (except E_c, which is insensitive to density changes) from the LDA are smaller in absolute magnitude than the corresponding exact values. Also, note that in Fig. 2 the LDA density is too small near the nucleus. The effect of the lower value of the GGA v_{xc} at short distances and of the negative divergence in the GGA v_{xc} at the nucleus is to increase the charge density near the nucleus and thereby increase the magnitude of all the components of the total energy. This explains why the GGAs yield not only improved values of E_{xc} but also modest improvements in other components of the total energy despite, or maybe one should say because of, the spurious divergence of v_{xc} at nuclei. In fact we have found the same to hold true for heavier atoms [21,28].

VII. DISCUSSION AND CONCLUSIONS

We have used very accurate wave functions for the helium isoelectronic series to calculate essentially exact values of several density-functional quantities, which are then used to test the accuracy of several approximate functionals. The Hartree-Fock density is more accurate than the LDA or GGA densities. Although the exchange and correlation energies calculated from the various GGAs (with the exception of the Langreth-Mehl GGA for heavy ions) are considerably more accurate than those from LDA, the situation is not as clear for the exchange and correlation potentials. The various GGA exchange functionals have certain features in common. They correctly lead to more negative total energies and reduced binding energies, relative to LDA, by favoring regions with large density gradients. They yield a lower potential than the LDA at short and intermediate distances from nuclei—a step in the right direction—but they also introduce a spurious divergence at the nuclei. Whereas the various GGA exchange functionals have some common features, the GGA correlation functionals are very different from each other and none of them yield correlation potentials that bear any resemblance to the true correlation potential.

Correlation is more subtle than exchange as manifested in several ways. (i) v_c can be either negative or positive in different regions of space whereas LDA can only give a negative v_c. (ii) For helium isoelectronic series, v_c varies less over space for heavy ions than for light atoms. This is also contradictory to the behavior in LDA. (iii) While v_c has qualitatively the same behavior for all members of the helium isoelectronic series (negative at short distances and long distance, positive at intermediate distances), it has qualitatively the opposite behavior [34] for the closely related model system of two electrons in a harmonic well.

The Perdew-Wang 1991 functional satisfies (see Table IV of Refs. [21] and [43]) more of the uniform scaling [40] and nonuniform scaling [41,42] conditions than the other functionals considered here. However, it does so in a somewhat tortured way that introduces spurious oscil-

TABLE III. Comparison of the self-consistent LDA (both Vosko-Wilk-Nusair and Perdew-Wang) and the Perdew-Wang 1991 GGA to the corresponding exact values for various components of the Kohn-Sham total energy, the density-weighted integral of v_{xc}, and the single-particle eigenvalue of He.

Property	LDA (VWN)	LDA (PW)	GGA (PW91)	Exact	Δ_{LDA} (PW)	Δ_{GGA} (PW91)
$E_{tot} = E^s_{kin} + E_{en} + E_H + E_{xc}$	-2.834 836	-2.834 455	-2.900 001	-2.903 724	0.069 269	0.003 723
E^s_{kin}	2.767 923	2.767 389	2.862 874	2.867 082	-0.099 693	-0.004 207
E_{en}	-6.625 564	-6.624 884	-6.737 527	-6.753 267	0.128 383	0.015 740
E_H	1.996 120	1.995 861	2.029 109	2.049 137	-0.053 276	-0.020 028
$E_{en} + E_H$	-4.629 444	-4.629 023	-4.708 420	-4.704 130	0.075 107	-0.004 290
E_x	-0.861 847	-0.861 740	-1.009 488	-1.024 568	0.162 828	0.015 080
E_c	-0.111 467	-0.111 080	-0.044 969	-0.042 107	-0.068 973	-0.002 862
$E_{xc} = E_x + E_c$	-0.973 314	-0.972 820	-1.054 457	-1.066 676	0.093 856	0.012 219
$\int d\mathbf{r}\, \rho(\mathbf{r})\, v_{xc}(\mathbf{r})$	-1.275 448	-1.274 739	-1.350 079	-2.019 537	0.744 798	0.669 458
ϵ_{1s}	-0.570 425	-0.570 256	-0.583 257	-0.903 724	0.333 468	0.320 467

lations of the potential near quadratic extrema of the charge density [34] and in the near tails of charge densities.

Since E_x and E_c are integrated quantities, it is possible for GGAs to improve upon them without making comparable improvements to v_x and v_c, which contain more detailed information. It is v_{xc} that controls the self-consistent charge densities. The electron-nucleus and Hartree energies E_{en} and E_H depend solely on the charge density. Since E_{en} and E_H have smaller errors in GGA than in LDA, by this measure, the GGA v_{xc} is a small improvement over the LDA v_{xc} despite the fact that the GGA v_{xc} has a spurious divergence.

None of the existing GGAs yield a potential with the correct long-distance asymptotic behavior of v_{xc} and none of them improve appreciably the energy of the highest occupied orbital, which equals the ionization energy for the true functional. Any GGA that includes derivatives of the density no higher than first order cannot simultaneously satisfy both the correct $-1/r$ behavior of v_{xc} and the correct $-1/(2r)$ behavior of ϵ_{xc} at large distances [10]. Further, we have shown in Sec. IV that any such GGA must have a spurious divergence in v_{xc} at nuclei. However, by including the Laplacian of the density in an appropriate way, it is possible to 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 [37]. We are presently searching for good parameter values in such a functional. The importance of Laplacian terms has also been recently pointed out by Engel and Vosko [44], who show that inclusion of Laplacian terms in a fourth-order gradient expansion (which does not correctly represent any of the above three asymptotic conditions) results in improved exchange potentials for atoms and jellium spheres.

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