Fourth-order gradient corrections to the exchange-only energy functional: Importance of $\nabla^2 n$ contributions

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The pertinence of fourth-order gradient corrections to the exchange-only energy functional $E_x[n]$ for producing accurate exchange potentials $v_x(\mathbf{r})$ is examined utilizing the exact $v_x(\mathbf{r})$'s obtained from the optimized-potential model (OPM) for spherical atoms and jellium spheres (whose inner regions have slowly varying densities for which the gradient expansion should be valid). It is found that the fourth-order contributions containing $\nabla^2 n$ represent important ingredients of $E_x[n]$ which should be included in gradient-based nonlocal extensions of the local-density approximation. In accordance with this observation the $v_x(\mathbf{r})$'s resulting from the fourth-order gradient expansion are closer to the exact $v_x^{\mathrm{OPM}}(\mathbf{r})$'s than those from generalized gradient approximations which do not contain $\nabla^2 n$ contributions.

I. INTRODUCTION

In recent years it has become clear that, while the local-density approximation (LDA) for the exchange-correlation energy functional $E_{\mathrm{xc}}[n_\uparrow, n_\downarrow]$ (the key ingredient of Kohn-Sham equations) has been very successful for a large variety of problems, the description of many interesting systems in atomic physics,[1–3] quantum chemistry,[4–7] and condensed matter physics,[8–15] requires nonlocal corrections to the LDA. The gradient expansion (GE), the most simple and systematic nonlocal extension of the LDA, has already been introduced in the seminal paper of Hohenberg and Kohn.[16] While the GE to second order (GE2) was found to be inadequate for the description of atoms (for an overview see Ref. 17) and few detailed investigations of its properties for solids (for which the GE should be more appropriate than for atoms) were performed, gradient corrected functionals have received renewed attention since the introduction of generalized gradient approximations (GGA's).[18–27] Such GGA's can be interpreted as partial resummations of the complete GE including only terms depending on ∇n but no higher gradients. While the expansion of GGA's for small gradients thus reproduces the GE2, it does not contain all fourth-order gradient corrections, which also depend on $\nabla^2 n$. In this paper we demonstrate that an inclusion of the $\nabla^2 n$ contributions of the GE clearly improves the ability of gradient based functionals to reproduce local quantities such as the exchange potential $v_x(\mathbf{r})$.

To this end we reconsider the GE to fourth order (GE4) for the exchange-only energy functional $E_x[n_\uparrow, n_\downarrow]$ first suggested by Herman, Van Dyke, and Ortenburger[28] for spin-compensated systems ($n/2 = n_\uparrow = n_\downarrow$),

$$E_x^{\mathrm{GE4}}[n] = \int d^3r \; e_x^{\mathrm{LDA}}(n)$$

$$\times \{1 + c_{x2}\xi + c_{x4}[\eta^2 + c_{\eta\xi}^x \eta\xi + c_{\xi^2}^x \xi^2]\} \quad (1.1)$$

where

$$e_x^{\mathrm{LDA}}(n) = -\frac{3k_F(\mathbf{r})}{4\pi} n(\mathbf{r}), \quad (1.2)$$

$$k_F(\mathbf{r}) \equiv [3\pi^2 n(\mathbf{r})]^{\frac{1}{3}}, \quad (1.3)$$

$$\xi(\mathbf{r}) \equiv \left(\frac{\nabla n(\mathbf{r})}{2k_F(\mathbf{r})n(\mathbf{r})}\right)^2, \quad (1.4)$$

$$\eta(\mathbf{r}) \equiv \frac{\nabla^2 n(\mathbf{r})}{4k_F^2(\mathbf{r})n(\mathbf{r})}. \quad (1.5)$$

Note that the corresponding spin-polarized functional can be directly obtained from (1.1) using the general property[29]

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2}\{E_x[2n_\uparrow] + E_x[2n_\downarrow]\}, \quad (1.6)$$

so that we restrict the discussion to $E_x[n]$ in the following.

The fact that, in spite of their early appearance in the literature, corrections depending on η have not been used in applications is mainly due to technical difficulties [compare the exchange potential from (1.1) given in Appendix A]. On one hand, only the GE's coefficients obtained from linear response,[30–33]

$$c_{x2} = \frac{10}{81}; \quad c_{x4} = \frac{146}{2025}, \quad (1.7)$$

are known exactly, but not the relative gradient co-efficients $c^x_{\eta\xi,\xi^2}$ which are determined by nonlinear response.[16,34,35] However, the values of $c^x_{\eta\xi,\xi^2}$ are restricted by the presently available information on the small momentum expansion of the relevant first-order three- and four-point functions to a narrow range,[35] the relative size of the q^4 coefficients being the only source of uncertainty. The most realistic values for $c^x_{\eta\xi,\xi^2}$ are obtained by the assumption that their relative size is identical to that of the corresponding coefficients of the noninteracting three- and four-point functions.[36–38] The resulting $c^x_{\eta\xi,\xi^2}$ are[35]

$$c^x_{\eta\xi} = -1.347; \quad c^x_{\xi^2} = 0.442, \qquad (1.8)$$

which is somewhat larger than the corresponding values for the kinetic energy functional $T_s[n]$.[39–41]

On the other hand, the fourth-order terms of Eq. (1.1) lead to divergent exchange energies for finite systems with exponentially decaying densities which makes it difficult to extract their relative contributions to E_x's for atoms unambigously. In this respect, however, recently some progress has been made[42] by use of a modified GE4 in the form of an extended GGA. In contrast to the initial suggestions[28] to overcome this problem, this approach is very much in the spirit of the GE and even allows higher-order contributions to the GE to be included approximately. Moreover, the exchange potential resulting from the GE4 diverges at the nuclear sites for point nuclei (although this divergence only shows up very close to the nucleus). This divergence, however, is easily eliminated by the (physically more correct) use of extended nuclei.

The present analysis is based on spherical atoms and jellium spheres (often used to model simple metal clusters[43–45] whose nomenclature is adopted here to distinguish them). Explicit results are given for Pd and Rn, which are characteristic of all atoms for which we have obtained optimized-potential-model (OPM) solutions,[46,27] and for the magic systems Na_{92} and Na_{254}, which are being characteristic of closed-shell jellium spheres. For the purpose at hand the region inside the jellium spheres provides a density which is very slowly varying [similar to the $n(r)$ in the interstitial region of solids] so that the GE should be valid. Only for these systems are optimized-potential-model[47,48] solutions available,[46] which (by the very definition of exchange-only[49,18,50]) represent the exact results within the exchange-only approximation and thus serve as an absolute standard for any approximate $E_x[n]$. In particular, OPM calculations provide the exact exchange potential $v_x(r)$ which is an ideal tool for analyzing $E_x[n]$ (Refs. 51, 46, and 27) as it gives much more detailed information than, e.g., the total E_x which (as an integral quantity) allows for fortuitous error cancellation. Moreover, in the present context $v_x(r)$ is the only unambigous quality criterion. In view of the inadequacy of the GE4 to deal with the asymptotic regime of these finite systems one is necessarily forced to analyze local quantities like the exchange energy density $e_x(r)$ or $v_x(r)$. But only $v_x(r)$ avoids all ambiguities arising from the nonuniqueness of the exchange energy den-

sity. As a functional derivative of (1.1) it is identical for all versions of $e_x(r)$ differing by partial integrations and thus allows for an examination of the interior of atoms and jellium spheres while ignoring the asymptotic regime which is irrelevant for solids.

It should be emphasized that atoms and jellium spheres complement one another in the sense that their geometry and characteristic scales are completely different. Basing an analysis on both systems provides information on the universality of approximate $E_x[n]$'s, i.e., it represents an additional check for fortuitous error cancellations. An approximate $E_x[n]$ which improves on the LDA/GE2 for both types of systems is much less likely to fail in real applications to solids than approximations solely constructed for only one particular type of system.

The paper is organized as follows. As a first step towards the analysis of the complete GE4 we consider (in Sec. II) a reduced fourth-order gradient expansion including only terms arising from linear response (LR4),

$$E^{LR4}_x[n] = \int d^3r \, e^{LDA}_x(n) \left\{ 1 + c_{x2}\xi + c_{x4}\eta^2 \right\} , \quad (1.9)$$

i.e., those ingredients of the GE4 whose coefficients are known exactly. It is found that the contribution of the fourth-order linear response term (η^2 term) to $v_x(r)$ is almost as large as that of the second-order correction for both atoms and jellium spheres. For the case of $T_s[n]$, however, substantial cancellation between the individual fourth-order terms occurs.[52] Thus, in Sec. III approximate values[35] for $c^x_{\eta\xi}$ and $c^x_{\xi^2}$ are used to show that cancellation effects between the η^2 contribution and the nonlinear response terms (which will be called the $\eta\xi$ and ξ^2 terms in the following) do not reduce the importance of the η contributions. Some details of our OPM results for jellium spheres are given in Appendix B.

II. η^2 CONTRIBUTION TO EXCHANGE POTENTIALS

The applicability and convergence of the GE is primarily based on the smallness of the successive terms in Eq. (1.1), i.e., on the size of ξ and η as well as similar ratios of higher gradients (Note, however, that at least to low order its convergence is also supported by the decreasing size with n of the prefactors c_{xn} of the nth order—in addition to $c_{x2} \approx 0.1234$ and $c_{x4} \approx 0.072$, the linear response contribution to the sixth order[33] is given by $c_{x6} = 38522/893025 \approx 0.043$). In order to judge the GE's usefulness and the importance of its various ingredients it is worth examining ξ and η for the systems under consideration. While ξ and η for Pd and Rn have been reported previously [Figs. (1a) and (1d) of Ref. 27], Figs. 1 and 2 show these quantities for Na_{92} and Na_{254} (together with the corresponding densities that illustrate the geometry of these systems — note that ξ has been enlarged by a factor of 10 to make it visible on this scale).

One first observes some similarities of ξ and η between atoms and jellium spheres: As already noted,[46] ξ and η decrease in the interior of these finite systems with
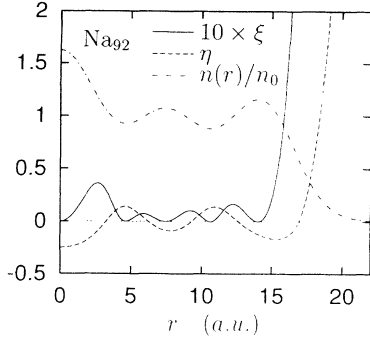
FIG. 1. ξ, Eq. (1.4), and η, Eq. (1.5), from OPM solutions for Na_{92} ($r_s = 3.93$, jellium radius $R = 17.741$ a.u.). To make ξ visible on this scale it has been multiplied by 10. Also the density $n(r)$ normalized to the corresponding bulk value is given for comparison.

increasing particle number, making Rn and Na_{254} particularly useful systems for the analysis of the GE. As for both atoms and jellium spheres, the density decays exponentially for large r and both ξ and η increase exponentially in the asymptotic regime. In solids, however, this regime is not present such that for our purposes only the interior of these finite systems is relevant. On the other hand, one notes fundamental differences between the two types of systems: While for atoms ξ and η are of similar magnitude, for clusters η is completely dominating, reflecting the fact that in their interior, jellium spheres should allow for a linear response treatment. Consequently, atoms and jellium spheres belong to completely different classes of systems and thus their combination represents a stringent test for any approximate $E_x[n]$. For both classes nonlocal corrections are required due to the very size of ξ (for atoms) and η (for atoms and jellium spheres). Moreover, while the r dependence of ξ and η is to some extent similar for atoms, these quantities are almost "orthogonal" for jellium spheres.

In this context it is important to realize that a somewhat similar behavior for ξ and η is found[53] in vanadium metal: In the interstitial region, η is much larger than ξ. Possibly of more importance is the large anisotropy of η, while ξ is essentially isotropic. From these results it is clear that η is much more important than ξ in the region
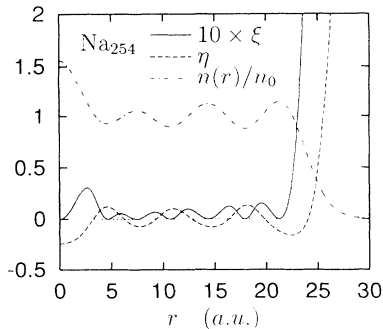

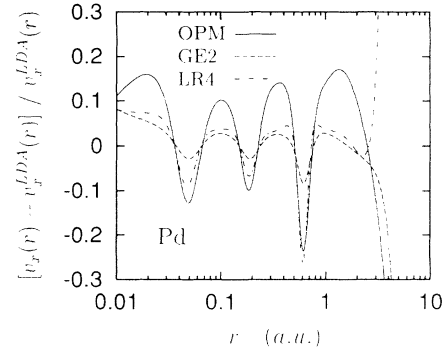FIG. 2. Same as Fig. 1 for Na_{254} ($r_s = 3.93$, jellium radius $R = 24.889$).

FIG. 3. Nonlocal contributions to the exchange potential of Pd from the GE2 and LR4, Eq. (1.9), obtained by insertion of the OPM density in comparison to the exact OPM result. $v_x^{OPM}(r)$ has been shifted by the difference between the highest occupied eigenvalues from the OPM and the LDA (see comment in Sec. II).

where metallization occurs. Analogous results demonstrating that η can be large in regions in which ξ almost vanishes have been found for CoO.[54]

In the following, the GE is compared to GGA's whose general form is given by

$$E_x^{GGA}[n] = \int d^3r \; e_x^{LDA}(n) \left[1 + c_{x2}g(\xi)\xi\right], \qquad (2.1)$$

where $g(\xi)$ is constructed such that the GGA exchange potential does not diverge for exponentially decaying densities. Thus GGA's can be understood as partial resummations of the complete GE. Note, however, that in constructing $g(\xi)$ one is not just attempting to make $g(\xi)$'s expansion in powers of ξ reproduce the ξ^n terms in the complete GE but, rather, is effectively trying to include all nonlocal contributions. From the comparison of Eqs. (1.1) and (2.1) it is thus obvious that GGA's are based on the assumption that all ingredients of the GE other than ξ and, in particular, η, can be approximately represented by simple powers of ξ. Thus GGA's should
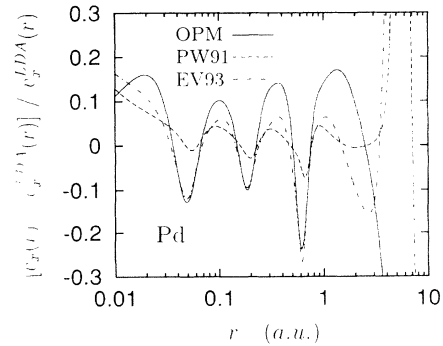

FIG. 4. Nonlocal contributions to the exchange potential of Pd from $PW91$ and $EV93$ obtained by insertion of the OPM density in comparison to the exact OPM result. $v_x^{OPM}(r)$ has been shifted by the difference between the highest occupied eigenvalues from the OPM and the LDA (see comment in Sec. II).
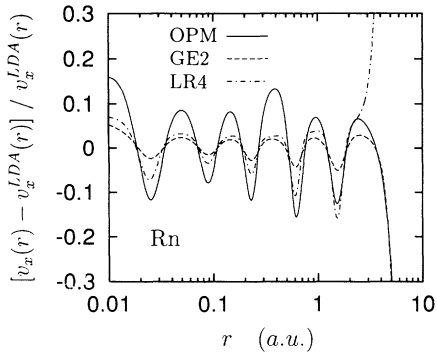
FOURTH-ORDER GRADIENT CORRECTIONS TO THE...

FIG. 5. Same as Fig. 3 for Rn.

FIG. 7. Same as Fig. 3 for Na$_{92}$.

only be expected to work for systems where this substitution is at least justified to a limited extent (as in atoms).

In Figs. 3–6 the nonlocal contributions to $v_x(r)$ from the GE2, LR4 (the potential resulting from the LR4/GE4 has been given by Herman, Van Dyke, and Ortenburger[28] — see also Appendix A) and two GGA's [PW91 (Ref. 23) and EV93 (Ref. 27)] are compared to the exact $v_x^{OPM}(r)$ for Pd and Rn. The potentials from the GE2, LR4, and the GGA's have been obtained by insertion of exact OPM densities. While ideally one would prefer to use v_x's from self-consistent calculations, it is well known that for the LDA and GGA's self-consistent and non-self-consistent atomic $v_x(r)$'s do not differ substantially. We expect an analogous behavior of v_x^{GE2} and v_x^{LR4} for extended systems. In order to correct the comparison of Figs. 3–6 for the deficiency of the LDA, GE2, LR4, and the GGA's to reproduce the asymptotic behavior of $v_x(r)$ for finite systems and thus the eigenvalues of highest occupied orbitals, the difference between the highest occupied OPM and LDA eigenvalues has been subtracted from $v_x^{OPM}(r)$, i.e., in all corresponding figures of this work the label OPM represents the shifted potential $v_x^{OPM}(r) - \epsilon_{hig.occ.}^{OPM} + \epsilon_{hig.occ.}^{LDA}$. This global shift resulting from the asymptotic regime is not relevant for the condensed matter systems one is finally aiming at. On the other hand, the relevant interior regime is more easily analyzed after taking out this global constant (compare the analogous plots for Pd and Rn without this correction in Ref. 27). From Figs. 3 and 5 it is obvious that the η^2 term contributes almost as much to $v_x(r)$ as the
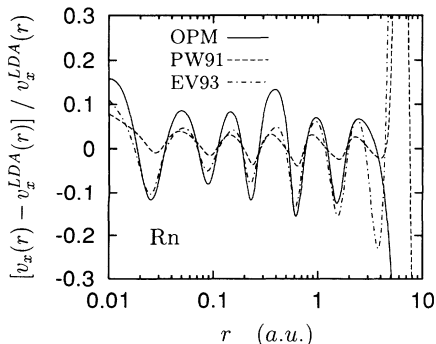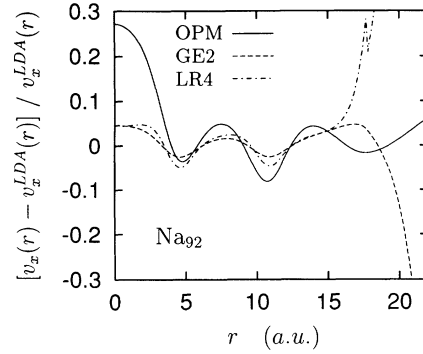
second-order ξ term and thus is by no means negligible. Comparing the GE2 and the LR4 to the GGA's whose $v_x(r)$'s are given in Figs. 4 and 6, one notes that while PW91 does not significantly improve $v_x(r)$ over the GE2, $v_x^{EV93}(r)$ is able to follow the nonlocal oscillations in the exact $v_x^{OPM}(r)$ much better[27], as one would expect from the method used for its construction. However, $v_x^{EV93}(r)$ is not really superior to $v_x^{LR4}(r)$.

In Figs. 7–10 the same comparison is made for Na$_{92}$ and Na$_{254}$. As far as the GE2 and LR4 are concerned, the picture is very similar to the atomic case: Again, the η^2 term clearly improves $v_x(r)$. [Note, however, that in accordance with the rather large η close to the origin (see Figs. 1 and 2), the LR4 is not able to reproduce the large nonlocal component of the exact $v_x^{OPM}(r)$ in this region.] The GGA's, on the other hand, show a different behavior than for atoms, which is due to their form for small ξ. While both PW91 and EV93 are restricted to the correct gradient coefficient c_{x2}, the way in which the two $g(\xi)$'s approach their limit $g(\xi = 0) = 1$ differs appreciably (see Fig. 2 of Ref. 27). Jellium spheres probe the regime $0 \le \xi < 0.05$ in which $g_{PW91}(\xi)$ rises from 1 to about 2.1, while $g_{EV93}(\xi)$ remains rather close to 1, i.e., to the GE2. As a consequence, PW91 oscillates between two gradient coefficients, i.e., c_{x2} and $2.1 \times c_{x2}$, and EV93 is more or less indistinguishable from the GE2. This failure of the GGA's to improve over the GE2 in a consistent way is directly related to the fact that for jellium spheres ξ and η are rather different, not only in size but also in shape. Thus, even a GGA that has been

FIG. 6. Same as Fig. 4 for Rn.
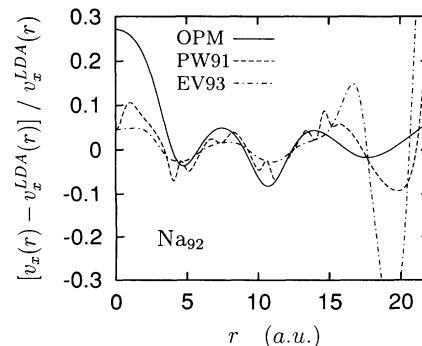
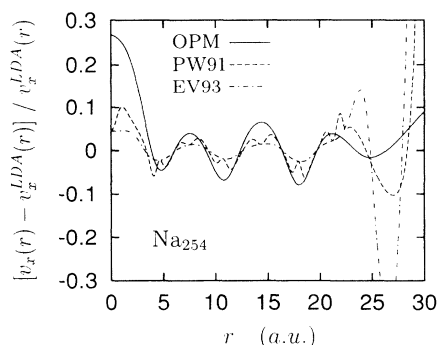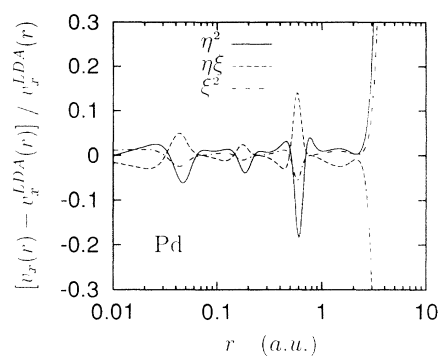FIG. 8. Same as Fig. 4 for Na$_{92}$.
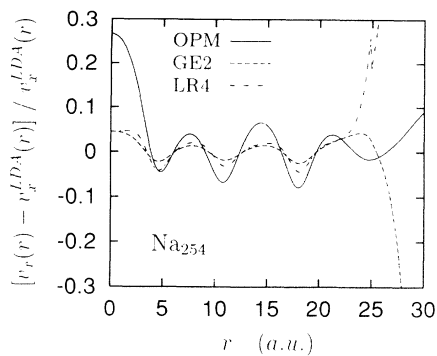
FIG. 9. Same as Fig. 3 for Na_{254}.

constructed to reproduce atomic $v_x(r)$'s as $EV93$ is not able to compensate for the missing η^2 contributions. The simple form of GGA's does not contain enough of the relevant characteristic density gradients to allow for a universally accurate functional.

From this comparison, it is obvious that for both types of systems the η^2 contribution is important. Taking together all systems considered for this study, LR4 approximates the exact $v_x^{OPM}(r)$ better than any GGA. Note that the independence of LR4's accuracy from the type of system considered reflects its systematic origin.

III. RESULTS FROM COMPLETE FOURTH-ORDER EXPANSION

Using the approximate $c_{\eta\xi}^x$ and $c_{\xi^2}^x$ from Eq. (1.8) one can check the importance of the $\eta\xi$ and ξ^2 terms relative to the η^2 term and the ability of the complete GE4 to reproduce $v_x^{OPM}(r)$. We start by separately plotting the contributions of the three terms to atomic $v_x(r)$'s in Figs. 11 and 12 (again obtained by insertion of exact OPM densities). From these figures it is obvious that in the interior of atoms the $\eta\xi$ term contributes almost as much as the η^2 term, while the ξ^2 contribution is somewhat smaller. However, due to their relative signs one finds considerable cancellation between the $\eta\xi$ and ξ^2 potentials. As a consequence, the complete $v_x^{GE4}(r)$ does not differ substantially from $v_x^{LR4}(r)$, as can be seen from the comparison of Figs. 3 and 5 with Figs. 13 and 14. In

FIG. 11. Nonlocal contributions to the exchange potential of Pd from the individual components of the GE4: η^2, $\eta\xi$, and ξ^2 contribution. For $c_{\eta\xi,\xi^2}^x$ the values of Eq. (1.8) have been used.

the latter, the $v_x^{GE4}(r)$'s resulting from two slightly different sets of relative gradient coefficients, the values of Eq. (1.8) (GE4a), and those for $T_s[n]$, i.e., $c_{\eta\xi}^x = -9/8$ and $c_{\xi^2}^x = 1/3$ (GE4b) are plotted together with the exact $v_x^{OPM}(r)$. Comparison of the two sets of $c_{\eta\xi,\xi^2}^x$ gives an estimate of the uncertainty left in the approximate evaluation of these coefficients. Figs. 13 and 14 show that both sets of relative gradient coefficients lead to almost identical $v_x(r)$'s (apart from the irrelevant asymptotic regime). Although this extreme agreement might be somewhat fortuitous, it seems that the accuracy to which $c_{\eta\xi}^x$ and $c_{\xi^2}^x$ is known is sufficient for actual applications of the GE4. Comparing either GE4a or GE4b with the LR4, Figs. 3 and 5, then demonstrates the net effect of the $\eta\xi$ and ξ^2 terms. In fact, the complete GE4 is very similar to the LR4. Consequently, the GE4 produces superior $v_x(r)$'s compared to $PW91$, while being almost as accurate as $EV93$ which was constructed from atomic $v_x^{OPM}(r)$ by use of the virial relation.

In Figs. 15 and 16 the individual fourth-order contributions are given for Na_{92} and Na_{254} (note the enlarged scale). These figures demonstrate explicitly that jellium spheres allow for a linear response treatment: The $\eta\xi$ and ξ^2 contributions to $v_x(r)$ are negligible, the η^2 term dominates completely. The resulting total $v_x^{GE4}(r)$'s are indistinguishable from the $v_x^{LR4}(r)$'s given in Figs. 7 and 9

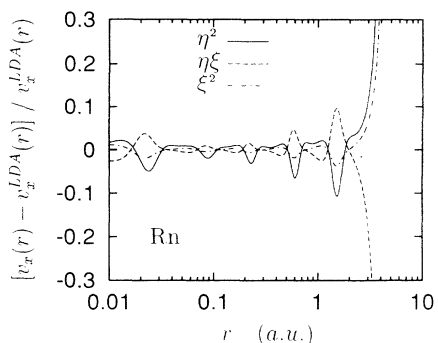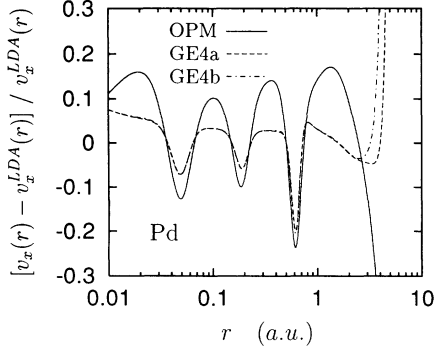FIG. 10. Same as Fig. 4 for Na_{254}.

FIG. 12. Same as Fig. 11 for Rn.

FIG. 13. Nonlocal contributions to the exchange potential of Pd from the OPM, and the GE4 using two different sets of $c^x_{\eta\xi,\xi^2}$: GE4a — $c^x_{\eta\xi,\xi^2}$ of Eq. (1.8), GE4b — $c^x_{\eta\xi} = -9/8$, $c^x_{\xi^2} = 1/3$. $v^{OPM}_x(r)$ has been shifted by the difference between the highest occupied eigenvalues from the OPM and the LDA (see comment in Sec. II).

so that we do not plot these potentials. As an immediate consequence, the conclusions from Sec. II concerning the LR4 are equally valid for the GE4, i.e., the GE4 turns out to be superior to both GGA's, which cannot adequately describe those systems in which η is much larger than ξ and the r dependence of η is very different from that of ξ.

IV. CONCLUDING REMARKS

In this paper it has been demonstrated that $\nabla^2 n$ contributions are important ingredients of the gradient expansion for $E_x[n]$. In fact, the $(\nabla^2 n)^2$ term contributes almost as much to the exchange potentials of atoms and jellium spheres as the second-order gradient correction. The need for inclusion of $\nabla^2 n$ terms in gradient based approximations to $E_x[n]$ is most obvious in regions in which ξ is small compared to η such that effectively the η^2 term represents the lowest-order inhomogeneity correction to the LDA (e.g., in the interior of jellium spheres and the interstitial region of solids as indicated by Singh's[53] results for V and Dufek, Blaha, and Schwarz's[54] results for CoO). Given the difficulties one faces when
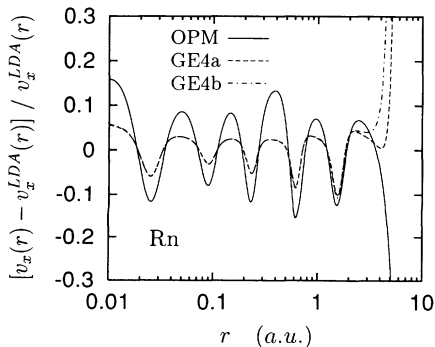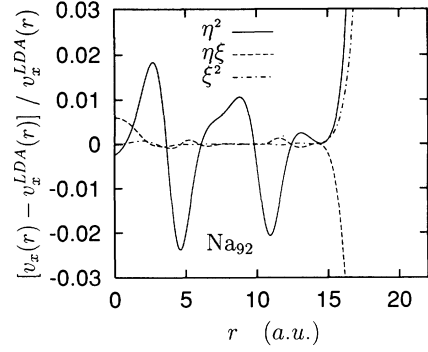

FIG. 15. Same as Fig. 11 for Na$_{92}$ (note the enlarged scale).

attempting to reproduce nonlocal contributions to exchange potentials,[27] this must be viewed as important information in spite of the remaining differences to the exact results.

The importance of $\nabla^2 n$-contributions is also reflected by the fact that the GE4 not only improves exchange potentials over the GE2 (as one might have expected) but is also superior to GGA's, which only contain first gradients of n. Fortunately, the concept of GGA's allows for the direct extension (GGA4) to include these contributions in the exchange kernel[42],

$$E^{GGA4}_x[n] = \int d^3r \; e^{LDA}_x(n) \; f(\xi, \eta) \quad ,$$

where for small ξ and η the GE4 should be reproduced,

$$f(\xi, \eta)1 + c_{x2}\xi + c_{x4}[\eta^2 + c^x_{\eta\xi}\eta\xi + c^x_{\xi^2}\xi^2] + \cdots \quad ,$$

and for large ξ or η the kernel $f(\xi, \eta)$ should be constructed such that the corresponding $v^{GGA4}_x(r)$ is finite for exponentially decaying densities (e.g., by using a Padé form similar to Ref. 42—the form of a corresponding GGA4 for $T_s[n]$ suggested in Ref. 55 seems to be too restricted). This extended form of GGA allows one to utilize $\nabla^2 n$ corrections also for systems with strongly inhomogeneous regions such as solids with localized orbitals or finite systems (e.g., molecules that have regions similar to the interstitial region of metals).

Nevertheless, as a first step towards a GGA4 it seems worth examining the properties of the GE4, Eq. (1.1), us-
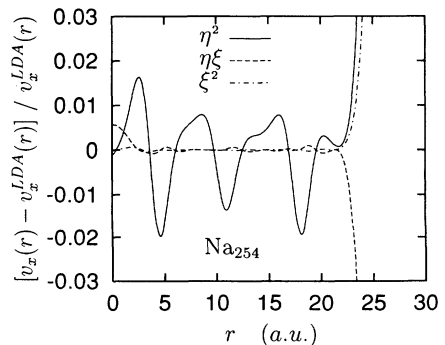

FIG. 14. Same as Fig. 13 for Rn.

FIG. 16. Same as Fig. 11 for Na$_{254}$ (note the enlarged scale).

ing the exact $c_{x2,x4}$, Eq. (1.7), and the approximate $c_{\eta\xi,\xi^2}^x$ of Eq. (1.8) in electronic structure calculations for metals. Since an equivalent analysis is not yet available for the correlation energy functional, we recommend combining the GE4 for $E_x[n]$ with the LDA for $E_c[n]$ for preliminary investigations of the effect of the η contributions.

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APPENDIX A: EXCHANGE POTENTIAL FROM GE4

For completeness, the potential arising from the GE4, Eq. (1.1), is given:

$$
\begin{aligned}
v_x^{GE4}(\mathbf{r}) = v_x^{LDA}(n)\Bigg\{ &1 + \frac{3}{2}\frac{c_{x2}}{(2k_F)^2}\left[-\frac{(\nabla^2 n)}{n} + \frac{2}{3}\frac{(\nabla n)^2}{n^2}\right] \\
&+ \frac{3}{2}\frac{c_{x4}}{(2k_F)^4}\Bigg[\left(\frac{(\nabla^4 n)}{n} - 4\sum_{i=1}^{3}\frac{(\partial_i n)(\partial_i \nabla^2 n)}{n^2} - 3\frac{(\nabla^2 n)^2}{n^2} + 6\frac{(\nabla^2 n)(\nabla n)^2}{n^3}\right) \\
&+ c_{\eta\xi}^x\left(-\frac{(\nabla^2 n)^2}{n^2} + \sum_{i,j=1}^{3}\frac{(\partial_i\partial_j n)(\partial_i\partial_j n)}{n^2} - 3\sum_{i=1}^{3}\frac{(\partial_i n)\partial_i(\nabla n)^2}{n^3} + 6\frac{(\nabla n)^4}{n^4}\right) \\
&+ c_{\xi^2}^x\left(-2\frac{(\nabla^2 n)(\nabla n)^2}{n^3} - 2\sum_{i=1}^{3}\frac{(\partial_i n)\partial_i(\nabla n)^2}{n^3} + 6\frac{(\nabla n)^4}{n^4}\right)\Bigg]\Bigg\},
\end{aligned} \tag{A1}
$$

where ∂_i denotes the partial derivative with respect to r_i. The potential for LR4 is obtained from Eq. (A1) by setting $c_{\eta\xi}^x = c_{\xi^2}^x = 0$. Note further that the exchange potential of spin-dependent systems,

$$
v_x^\sigma([n_\sigma], \mathbf{r}) = \frac{\delta}{\delta n_\sigma(\mathbf{r})} E_x[n_\uparrow, n_\downarrow] \quad,
$$

can be obtained from the spin-compensated $v_x(\mathbf{r}) = v_x([n], \mathbf{r})$, Eq. (A1), using (1.6),

TABLE I. Total ground state energies E_{tot}, total exchange energies E_x, eigenvalues of highest occupied orbital ϵ_{mk} (in hartrees), and differences between E_x and the right-hand side of the exchange virial relation, Eq. (B1), (in mhartrees) from numerical OPM calculations for closed-shell jellium spheres ($r_s = 3.93$).

Size	$-E_{\text{tot}}$ (hartrees)	$-E_x$ (hartrees)	$-\epsilon_{mk}$ (hartrees)	Error (mhartrees)
2	0.0994	0.2214	0.1813	0.0001
8	0.3735	0.8799	0.1626	0.0001
18	0.8074	2.0177	0.1444	-0.0014
20	0.8978	2.1987	0.1300	-0.0004
34	1.5247	3.8435	0.1331	-0.0043
40	1.7460	4.4018	0.1207	0.0001
58	2.6088	6.5650	0.1271	0.0042
92	4.1317	10.4056	0.1273	0.0106
138	6.1615	15.5893	0.1150	0.0182
186	8.3117	21.2070	0.1168	0.0334
198	8.7645	22.3432	0.1017	0.0243
254	11.3572	28.9642	0.1141	0.0526

$$
\begin{aligned}
v_x^\sigma([n_\sigma], \mathbf{r}) &= \frac{\delta}{\delta(2n_\sigma(\mathbf{r}))}\Big\{E_x[2n_\uparrow] + E_x[2n_\downarrow]\Big\} \\
&= v_x([2n_\sigma], \mathbf{r}).
\end{aligned}
$$

APPENDIX B: OPM RESULTS FOR JELLIUM SPHERES

In this Appendix we give some further information on our OPM solutions for jellium spheres (with $r_s = 3.93$). In Table I the total ground state energies, total E_x's, and the eigenvalues of the highest occupied orbitals are listed for a number of closed-shell systems. As already emphasized earlier,[46] the virial relation for $E_x[n]$ (Ref. 56; see also Ref. 57),

$$
E_x[n] = \int d^3r \; v_x(\mathbf{r})\Big[3n(\mathbf{r}) + \mathbf{r}\cdot\nabla n(\mathbf{r})\Big], \tag{B1}
$$

is also valid for external potentials for which the conventional virial theorem $V = -2T$ does not hold (as, e.g., jellium spheres) and provides an ideal quality criterion for OPM solutions for finite systems. Thus, in order to demonstrate the accuracy of our OPM solutions for jellium spheres, the difference between E_x and the right-hand side of Eq. (B1) evaluated using the numerical $v_x^{OPM}(r)$ is also listed in Table I. Even for the largest systems, this error is 2×10^{-6} smaller than the corresponding E_x^{OPM}, which is the same relative accuracy as obtained for spherical atoms.[46]

[1] J. Harris and R. O. Jones, J. Chem. Phys. **68**, 3316 (1978); **70**, 830 (1979).

[2] J. B. Lagowski and S. H. Vosko, Phys. Rev. A **39**, 4972 (1989).

[3] R. E. Watson, G. W. Fernando, M. Weinert, Y. J. Wang, and J. W. Davenport, Phys. Rev. B **43**, 1455 (1991).

[4] F. W. Kutzler and G. S. Painter, Phys. Rev. Lett. **59**, 1285 (1987).

[5] A. D. Becke, in *The Challenge of d and f Electrons: Theory and Computation*, edited by D. R. Salahub and M. C. Zerner (American Chemical Society, Washington, D.C., 1989), p. 165.

[6] P. Mlynarski and D. R. Salahub, Phys. Rev. B **43**, 1399 (1991).

[7] G. Ortiz and P. Ballone, Phys. Rev. B **43**, 6376 (1991); Z. Phys. D **19**, 169 (1991).

[8] C. S. Wang, B. M. Klein, and H. Krakauer, Phys. Rev. Lett. **54**, 1852 (1985).

[9] H. J. F. Jansen, K. B. Hathaway, and A. J. Freeman, Phys. Rev. B **30**, 6177 (1984); K. B. Hathaway, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **31**, 7603 (1985).

[10] X. J. Kong, C. T. Chan, K. M. Ho, and Y. Y. Ye, Phys. Rev. B **42**, 9357 (1990).

[11] G. Ortiz, Phys. Rev. B **45**, 11 328 (1992).

[12] A. Garcia, Ch. Elsässer, J. Zhu, S. G. Louie, and M. L. Cohen, Phys. Rev. B **46**, 9829 (1992); **47**, 4150(E) (1993).

[13] K. Kikuchi, T. Uda, A. Sakuma, M. Hirao, and Y. Murayama, Solid State Commun. **81**, 653 (1992).

[14] T. C. Leung, C. T. Chan, and B. N. Harmon, Phys. Rev. B **44**, 2923 (1991).

[15] D. J. Singh, W. E. Pickett, R. E. Cohen, D. A. Papaconstantopoulos, and H. Krakauer, Physica B **163**, 470 (1990).

[16] P. Hohenberg and W. Kohn, Phys. Rev. **136B**, 864 (1964).

[17] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).

[18] D. C. Langreth and M. J. Mehl, Phys. Rev. B **28**, 1809 (1983).

[19] A. D. Becke, J. Chem. Phys. **84**, 4524 (1986).

[20] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[21] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).

[22] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986); **34**, 7406(E) (1986).

[23] J. P. Perdew, in *Electronic Structure of Solids 1991*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), Vol. 11.

[24] S. H. Vosko and L. D. Macdonald, in *Condensed Matter Theories*, edited by P. Vashishta, R. K. Kalia, and R. F. Bishop (Plenum, New York, 1987), Vol. 2, p.101.

[25] A. E. DePristo and J. D. Kress, J. Chem. Phys. **86**, 1425 (1987).

[26] D. J. Lacks and R. G. Gordon, Phys. Rev. A **47**, 4681 (1993).

[27] E. Engel and S. H. Vosko, Phys. Rev. B **47**, 13 164 (1993).

[28] F. Herman, J. P. Van Dyke, and I. B. Ortenburger, Phys. Rev. Lett. **22**, 807 (1969); F. Herman, I. B. Ortenburger, and J. P. Van Dyke, Int. J. Quant. Chem. **IIIS**, 827 (1970).

[29] G. L. Oliver and J. P. Perdew, Phys. Rev. A **20**, 397 (1979).

[30] P. R. Antoniewicz and L. Kleinman, Phys. Rev. B **31**, 6779 (1985).

[31] L. Kleinman and S. Lee, Phys. Rev. B **37**, 4634 (1988).

[32] J. A. Chevary and S. H. Vosko, Bull. Am. Phys. Soc. **33**, 238 (1988); Phys. Rev. B **42**, 5320 (1990).

[33] E. Engel and S. H. Vosko, Phys. Rev. B **42**, 4940 (1990); **44**, 1446(E) (1991).

[34] D. J. W. Geldart and M. Rasolt, in *Single-Particle Density in Physics and Chemistry*, edited by N. H. March and B. M. Deb (Academic Press, London, 1987), p.151.

[35] E. Engel and S. H. Vosko (unpublished).

[36] P. Lloyd and S. A. Sholl, J. Phys. C **1**, 1620 (1968).

[37] E. G. Brovman and Yu. Kagan, Zh. Eksp. Teor. Fiz. **63**, 1937 (1972) [Sov. Phys. JETP **36**, 1025 (1973)].

[38] E. G. Brovman and A. Kholas, Zh. Eksp. Teor. Fiz. **66**, 1877 (1974) [Sov. Phys. JETP **39**, 924 (1974)].

[39] D. A. Kirzhnits, Zh. Eksp. Teor. Fiz. **32**, 115 (1957) [Sov. Phys. JETP **5**, 64 (1957)]; *Field Theoretical Methods in Many-Body Systems* (Pergamon, London, 1967).

[40] C. H. Hodges, Can. J. Phys. **51**, 1428 (1973).

[41] B. K. Jennings, Ph.D. thesis, McMaster University, 1973; M. Brack, B. K. Jennings, and Y. H. Chu, Phys. Lett. **65B**, 1 (1976).

[42] S. H. Vosko, L. D. Macdonald, and E. Engel, Bull. Am. Phys. Soc. **36**, 662 (1991).

[43] W. Ekardt, Phys. Rev. B **29**, 1558 (1984).

[44] D. E. Beck, Solid State Commun. **49**, 381 (1984).

[45] M. Y. Chou, A. Cleland, and M. L. Cohen, Solid State Commun. **52**, 645 (1984).

[46] E. Engel and S. H. Vosko, Phys. Rev. A **47**, 2800 (1993).

[47] R. T. Sharp and G. K. Horton, Phys. Rev. **90**, 317 (1953).

[48] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).

[49] V. Sahni, J. Gruenebaum, and J. P. Perdew, Phys. Rev. B **26**, 4371 (1982).

[50] L. J. Sham, Phys. Rev. B **32**, 3876 (1985).

[51] E. Engel, J. A. Chevary, L. D. Macdonald, and S. H. Vosko, Z. Phys. D **23**, 7 (1992).

[52] J. S.-W. Wang and M. Rasolt, Phys. Rev. B **13**, 5330 (1976).

[53] D. J. Singh (private communication).

[54] P. Dufek, P. Blaha, and K. Schwarz (private communication).

[55] G. I. Plindov and S. K. Pogrebnya, Chem. Phys. Lett. **143**, 535 (1988).

[56] M. Levy and J. P. Perdew, Phys. Rev. A **32**, 2010 (1985).

[57] S. K. Ghosh and R. G. Parr, J. Chem. Phys. **82**, 3307 (1985).