Gradient expansion for $T_s[n]$: Convergence study for jellium spheres

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The convergence of the gradient expansion (GE) for the kinetic energy functional $T_s[n]$ is tested on the basis of the spherical jellium model for metal clusters. By insertion of Kohn-Sham densities into the GE it is found that fourth-order contributions to the GE are more important for jellium spheres than for atoms, indicating that these corrections might also be relevant for the description of solids. By solution of the Euler-Lagrange equations resulting from the GE truncated at second or fourth order, it is demonstrated that the variational accuracy of the GE is considerably lower than that obtained by insertion of high-quality densities. Furthermore, it is shown that a GE to second order with an adjusted prefactor of the gradient term does not give variational results for jellium spheres superior to a fourth-order GE as in the case of atoms.

The construction of nonlocal corrections to the exchange-correlation energy functional $E_{xc}[n]$ is one of the key issues of density-functional theory (DFT). Among the various suggestions for nonlocal approximations to $E_{xc}[n]$ the gradient expansion (GE) as the most direct extension of the local-density approximation (LDA) was the first to be considered in the literature.[1-4] However, applications of second-order gradient corrections to atoms seemed to demonstrate the inadequacy of the GE, at least for these finite systems. By now it is clear that part of the failure of the second-order gradient correction to the exchange-only $E_x[n]$ was due to the incorrect gradient coefficient used.[5] Moreover, it has recently been argued[6] that fourth-order contributions are important ingredients of the GE for $E_x[n]$ such that it seems worth to examine the GE's properties for extended systems, i.e., solids, in more detail.

In contrast to the limited information available on the GE for $E_{xc}[n]$ (concerning both gradient coefficients and properties in applications) much more is known about the corresponding GE for the kinetic energy functional $T_s[n]$. In addition to the second-order gradient correction[7,8,1] $T_s^{[2]}[n]$ the fourth-[7,9,10] ($T_s^{[4]}[n]$) and sixth-order[11] contributions have been evaluated. Furthermore, in contrast to the corresponding fourth-order correction for exchange $T_s^{[4]}[n]$ is finite for exponentially decaying densities such that not only the second-order GE (GE2),

$$T_s^{GE2}[n] = T_s^{[0]}[n] + T_s^{[2]}[n],$$

$$T_s^{[0]}[n] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int d^3r \; n^{\frac{5}{3}},$$

$$T_s^{[2]}[n] = \frac{\lambda}{8} \int d^3r \; \frac{(\nabla n)^2}{n},$$

($\lambda = 1/9$ within the GE) but also the fourth-order (GE4),

$$T_s^{GE4}[n] = T_s^{GE2}[n] + T_s^{[4,1]}[n] + T_s^{[4,2]}[n] + T_s^{[4,3]}[n],$$

$$T_s^{[4,1]}[n] = \frac{1}{540(3\pi^2)^{\frac{2}{3}}} \int d^3r \; n^{\frac{1}{3}} \left(\frac{\nabla^2 n}{n}\right)^2,$$

$$T_s^{[4,2]}[n] = -\frac{1}{480(3\pi^2)^{\frac{2}{3}}} \int d^3r \; n^{\frac{1}{3}} \left(\frac{\nabla^2 n}{n}\right)\left(\frac{\nabla n}{n}\right)^2,$$

$$T_s^{[4,3]}[n] = \frac{1}{1620(3\pi^2)^{\frac{2}{3}}} \int d^3r \; n^{\frac{1}{3}} \left(\frac{\nabla n}{n}\right)^4,$$

has been extensively tested for atoms.[12-17] The information on the GE4 for $T_s[n]$ provides an idea of what can be expected from the GE4 for $E_{xc}[n]$.

It is not clear, however, how well results for atoms characterize the situation in solids for which the GE should be more appropriate. It is thus worthwhile to analyze the GE's properties for other model systems in order to check the universal significance of the results found for atoms. Particularly interesting in this respect are systems which show an extended weakly inhomogeneous region (analogous to the interstitial region in metals) but allow for an exact treatment in order to have a rigorous comparative standard. One such system is the spherical jellium model for metal clusters[18-20] on which the present study is based. In this model the ionic structure of metal clusters (whose nomenclature is adopted here) is approximated by a homogeneous background charge density $n_+(r) = n_0 \Theta(R - |r|)$ characterized by the bulk Wigner-Seitz radius $r_S = (3/4\pi n_0)^{\frac{1}{3}}$ and the cluster radius $R = r_S N^{\frac{1}{3}}$. While shell effects remain present for all the cluster sizes considered here (ranging from Na_2 to Na_{254}), the density in the interior of these jellium spheres systematically approaches the homogeneous limit with increasing size (compare Ref. 18) thus covering density gradients complementary to those found in atoms.[6]

Moreover, while a variety of even more nonlocal approximations to $T_s[n]$ have been discussed in the literature (see, e.g., Refs. 15, 21–24), the original GE (to either second or fourth order) has been the only form used for real applications in atomic,[25] surface,[26-28] and nuclear physics (for a review see Ref. 29). Renewed interest in the GE originates from the growing field of cluster physics where the jellium model has been extensively applied to discuss global trends for ground state properties and collective excitations. In this context the GE has, e.g., been used to evaluate the size dependence of electronic properties of clusters (see, e.g., Refs. 30–34 — establishing the liquid drop model for metal clusters[35]) and the stability of charged clusters.[36,37] However, to date no systematic study of the convergence of the GE for these systems is available. In particular, the importance of fourth-order contributions which turned out to be necessary for the realistic description of nuclei[29] (whose geometry is rather similar to that of jellium spheres) and surfaces[38] has not

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been studied in detail. Thus in addition to the conceptual reasons for examining the GE for jellium spheres its properties for these systems are also of practical interest.

For a comparison of the GE with the exact $T_s[n]$ using jellium spheres we follow the two routes previously exploited in the atomic situation: (i) By insertion of "exact" densities into the various orders $T_s^{[i]}[n]$ the convergence of the GE is investigated. In the present context the results of Kohn-Sham (KS) calculations for jellium spheres using an accurate form[39] of the LDA for $E_{xc}[n]$ serve as an "exact" reference standard. (ii) By solving the Euler-Lagrange equations resulting from the GE2/4 for $T_s[n]$ in combination with $E_{xc}^{LDA}[n]$,

$$\frac{\delta E[n]}{\delta n(r)} = \mu, \tag{1}$$

$$E[n] = T_s^{GE2/4}[n] + E_{es}[n] + E_{xc}^{LDA}[n],$$

$$E_{es}[n] = \frac{1}{2} \int d^3r \int d^3r'$$
$$\times \frac{[n(r) - n_+(r)]\,[n(r') - n_+(r')]}{|r - r'|},$$

the variational properties of the GE2/4 are tested. Note that in order to examine the GE for $T_s[n]$ an approximate $E_{xc}[n]$ is completely legitimate as long as the same $E_{xc}[n]$ is used with the GE and the reference standard.

In Table I the $T_s^{[i]}[n]$ obtained by insertion of KS densities for a number of closed-shell jellium spheres (for sodium, $r_S = 3.93$ a.u.) are compared with the corresponding exact T_s. The fourth-order contribution has been decomposed into its three components in order to reveal the relative size of the ∇n and $\nabla^2 n$ contributions. Furthermore, the percentage errors δ_i of the GE0 (i.e., the Thomas-Fermi approximation), the GE2, and the GE4 are listed. In Table II the corresponding energies and errors for closed-shell atoms are given (here densities and energies from exchange-only LDA calculations have been utilized — note that neither the relative size of the $T_s^{[i]}$ nor the δ_i depend on the specific reference densities used for this comparison).

First of all, one notes that the accuracy of $T_s^{[0]}$ becomes

higher with increasing size of both clusters and atoms. Comparing both types of systems it seems that the error of the GE0 is almost a factor of 2 lower for jellium spheres (2.9% for Na$_{92}$ versus 4.5% for Rn). The picture is completely different for the GE2. On one hand δ_2 does not vary as much as δ_0 with increasing electron number. While one notices some decrease with electron number for jellium spheres (1.3% for Na$_{18}$ compared to 0.7% for Na$_{254}$), δ_2 is rather independent of the size of atoms (with the exception of the very small atoms). Moreover, the ratio $T_s^{[2]}/T_s^{[0]}$ is considerably smaller for jellium spheres (1/60) than for atoms (1/25) and δ_2 is somewhat larger. The most pronounced differences between jellium spheres and atoms, however, are found for the GE4. Already the relative size of $T_s^{[4]}$ and $T_s^{[2]}$ indicates the importance of fourth-order contributions for jellium spheres: $T_s^{[4,1]}$ and $T_s^{[4,2]}$ are roughly twice as large as $T_s^{[2]}$, while $T_s^{[4,3]}$ is about as large. In spite of a large degree of cancellation between the three fourth-order contributions their sum still represents about one-third of $T_s^{[2]}$. In atoms, on the other hand, $T_s^{[2]}$ dominates completely over all individual fourth-order terms and their sum. In accordance with this observation one notices that the accuracy of the GE4 is clearly higher for atoms where errors of less than 0.1% indicate "convergence" of the GE. While the improvement over the GE2 offered by the GE4 is less impressive for jellium spheres (errors are reduced by roughly a factor of 3), the size of the fourth-order terms nevertheless requires their inclusion. Moreover, for both atoms and jellium spheres $T_s^{[4,1]}$ and $T_s^{[4,2]}$ dominate over $T_s^{[4,3]}$ (compare the corresponding contributions to surface energies given in Ref. 38).

In Fig. 1 the solutions of Eq. (1) for Na$_{92}$ are compared with the corresponding KS density. As is well known from atoms and nuclei the GE2/4 are not able to reproduce any shell structure but rather average through the shell oscillations of the exact density. Figure 1 demonstrates, however, that the surface region is more accurately described by the GE4 than by the GE2, corroborating the importance of fourth-order corrections from a local perspective. Note that asymptotically GE4 den-

TABLE I. Individual contributions $T_s^{[i]}$ to the GE for $T_s[n]$ obtained by insertion of KS densities and corresponding percentage deviations δ_i from exact KS result, T_s^{KS}, for closed-shell jellium spheres with $r_S = 3.93$ a.u. (all energies in hartrees).

Size	T_s^{KS}	$T_s^{[0]}$	δ_0	$T_s^{[2]}$	δ_2	$T_s^{[4,1]}$	$T_s^{[4,2]}$	$T_s^{[4,3]}$	δ_4
2	0.115	0.105	8.81	0.013	-2.31	0.037	-0.051	0.021	-7.56
8	0.493	0.463	6.04	0.029	0.18	0.072	-0.096	0.037	-2.29
18	1.171	1.107	5.50	0.049	1.33	0.103	-0.136	0.051	-0.20
20	1.275	1.210	5.06	0.049	1.21	0.104	-0.137	0.051	-0.23
34	2.259	2.157	4.53	0.073	1.28	0.144	-0.188	0.069	0.14
40	2.611	2.486	4.77	0.074	1.95	0.141	-0.183	0.067	0.96
58	3.885	3.746	3.56	0.102	0.93	0.200	-0.256	0.093	-0.02
92	6.192	6.011	2.92	0.135	0.73	0.256	-0.325	0.117	-0.03
132	8.998	8.734	2.93	0.173	1.01	0.317	-0.400	0.143	0.34
138	9.331	9.089	2.60	0.172	0.77	0.310	-0.391	0.139	0.14
186	12.725	12.402	2.54	0.215	0.85	0.386	-0.484	0.172	0.27
196	13.335	13.003	2.49	0.213	0.89	0.370	-0.463	0.164	0.36
198	13.461	13.119	2.54	0.211	0.97	0.363	-0.454	0.161	0.45
254	17.418	17.033	2.21	0.261	0.71	0.461	-0.574	0.203	0.20

TABLE II. Individual contributions $T_s^{[i]}$ to the GE for $T_s[n]$ obtained by insertion of KS densities and corresponding percentage deviations δ_i from exact KS result, T_s^{KS}, for closed-shell atoms (all energies in hartrees).

Atom	T_s^{KS}	$T_s^{[0]}$	δ_0	$T_s^{[2]}$	δ_2	$T_s^{[4,1]}$	$T_s^{[4,2]}$	$T_s^{[4,3]}$	δ_4
He	-2.724	2.411	11.48	0.303	0.37	0.216	-0.274	0.136	-2.47
Be	-14.223	12.766	10.24	1.479	-0.15	0.510	-0.507	0.326	-2.47
Ne	-127.491	116.516	8.61	9.933	0.82	2.049	-1.358	1.206	-0.67
Mg	-198.249	182.471	7.96	14.568	0.61	2.675	-1.484	1.526	-0.76
Ar	-524.517	487.449	7.07	34.000	0.58	5.714	-2.592	3.017	-0.59
Ca	-674.160	627.254	6.96	42.374	0.67	6.847	-2.800	3.539	-0.45
Zn	-1773.910	1661.010	6.36	97.151	0.89	13.992	-4.189	6.872	-0.05
Kr	-2746.866	2585.381	5.88	141.292	0.74	19.740	-5.271	9.441	-0.14
Sr	-3125.998	2945.731	5.77	157.952	0.71	21.776	-5.477	10.319	-0.14
Pd	-4931.010	4663.183	5.43	233.783	0.69	31.385	-6.975	14.482	-0.10
Cd	-5457.822	5165.591	5.35	255.153	0.68	34.042	-7.314	15.609	-0.10
Xe	-7223.657	6848.711	5.19	324.938	0.69	42.748	-8.466	19.265	-0.05
Ba	-7874.734	7468.701	5.16	350.153	0.71	45.766	-8.699	20.506	-0.02
Yb	-13380.911	12726.033	4.89	550.976	0.78	69.370	-10.748	30.441	0.11
Pt	-17318.534	16509.127	4.67	686.767	0.71	85.309	-12.111	37.033	0.07
Hg	-18395.920	17545.544	4.62	723.202	0.69	89.568	-12.431	38.772	0.06
Rn	-21852.321	20869.844	4.50	838.258	0.66	103.082	-13.530	44.258	0.05

sities vanish like $1/r^6$ (see, e.g., Ref. 17), while GE2 densities decay exponentially. This property, however, does only show up[17] for extremely large r and thus does not affect the behavior of $n(r)$ in the physically relevant part of the asymptotic regime (1–4 a.u. in the case of atoms). This is reflected by the fact that chemical potentials from GE4 calculations are superior to their GE2 counterparts (e.g., for Na$_{92}$ one obtains $\mu_{GE4} = 0.0957$ a.u. and $\mu_{GE2} = 0.0871$ a.u. compared to the eigenvalue of the highest occupied KS orbital of 0.1124 a.u.).

In Fig. 2 the percentage errors of ground state energies from variational calculations using $T_s^{GE2/4}[n]$ are plotted for Na$_2$ to Na$_{254}$. Quite generally the GE2/4 lead to an overbinding compared to KS ground state energies. Moreover, the GE2/4 do not reproduce any shell structure and the ground state energies per particle are monotonically increasing with electron number for both variants. Consequently one observes the magic numbers (8,18,20,34,...) corresponding to shell closings of particularly stable shells in the case of KS calculations as min-

ima in the GE's error. The overall level of accuracy of the GE's variational energies is comparable to that for atoms (compare Fig. 2 of Ref. 17). While for very small systems the error can be of the order of 10%, it is systematically decreasing with increasing particle number (although rather slowly). Errors of about 2–4% for the GE2 and 1–2% for the GE4 are typical for most of the systems considered here. As for atoms the errors from variational use of the GE2/4 are considerably higher than those obtained by insertion of "good" densities. However, the former accuracy is more characteristic of what one can expect from applications of the GE2/4.

In the atomic case it has been shown[40] that a modified GE2 with a prefactor $\lambda = 1/5$ generates very accurate atomic ground state energies over the complete periodic table. This can be understood on the basis of Lieb's proof[41] that the leading two terms in a $1/N^{\frac{1}{3}}$ expansion of the exact ground state energy of neutral atoms are reproduced by variational solutions from the GE2 if $\lambda =$
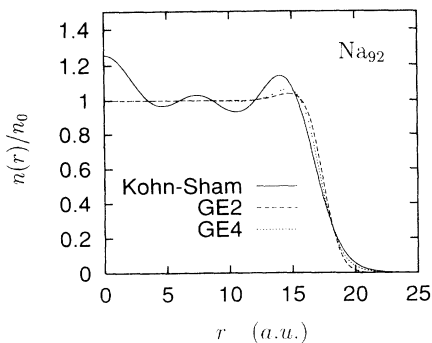

FIG. 1. Density profiles for Na$_{92}$ from Kohn-Sham calculation (solid line) and solution of (1) (GE2 — dashed line, GE4 — dotted line).
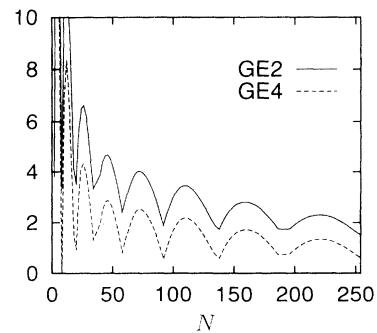

FIG. 2. Percentage deviation of ground state energies for jellium spheres ($r_S = 3.93$ a.u.) obtained by solution of (1) (GE2 — solid line, GE4 — dashed line) from KS ground state energies.

0.1859... is used. The corresponding expansion of the ground state energy of jellium spheres,

$$E(R) = \frac{4\pi}{3} R^3 \, \alpha + 4\pi R^2 \, \sigma + 2\pi R \, \gamma + \cdots \quad , \quad (2)$$

where α represents the bulk energy density of the corresponding metal, σ is the surface, and γ the curvature energy, constitutes the liquid drop model for metal clusters.[35] In analogy to the atomic case one can try to reproduce the "exact" σ obtained from KS calculations for the planar surface by the GE2 adjusting λ appropriately. In fact, choosing $\lambda = 0.2179$ (for $r_S = 4$ a.u.) and evaluating the coefficients of the expansion (2) as in Ref. 32 one obtains $\sigma = 163.5$ ergs/bohr^2, i.e., exactly the planar surface value.[42] The accuracy of the corresponding ground state energies for small jellium spheres is given in Fig. 3. As in the atomic situation the errors of this modified GE2 are smaller than those of the original GE2 and seem to approach zero for large systems. However, unlike the atomic case the absolute size of the errors remains of the order of 1% even for rather large systems due to the pronounced shell structure. Moreover, the value of λ which reproduces the exact σ depends on the jellium density r_S. Chizmeshya and Zaremba[27] have analyzed the r_S dependence of λ by applying the modified GE2 to the planar surface problem. They found that $1/4$ is the optimum value for λ taking into account
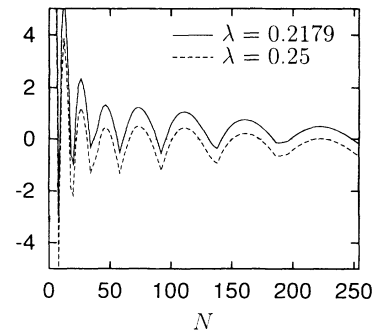

FIG. 3. Percentage deviation of ground state energies for jellium spheres ($r_S = 4$ a.u.) obtained by solution of (1) (GE2 with $\lambda = 0.2179$ — solid line, GE2 with $\lambda = 0.25$ — dashed line) from KS ground state energies.

the density range r_S=2–6 a.u. In Fig. 3 the errors for this choice of λ are also plotted. While one notices a tendency of $\lambda = 1/4$ to underbind, the overall accuracy with this prefactor is only marginally worse than that of $\lambda = 0.2179$ such that this more universal choice seems to be preferable to an individual adjustment of λ to the r_S considered. Nevertheless the modified GE2 does not represent such an attractive alternative to the GE4 for jellium spheres as it does for atoms.

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