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Exact exchange-only potentials and the virial relation as microscopic criteria for generalized gradient approximations

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The information contained in the exact exchange potential of atoms as calculated in the optimized-potential model is used to analyze generalized gradient approximations (GGA's) from a microscopic viewpoint. It is shown that the GGA recently introduced by Perdew and Wang [in *Electronic Structure of Solids 1991*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), Vol. 11] does not significantly improve the exchange potential given by the lowest-order gradient correction. This contrasts with its excellent reproduction of atomic exchange energies, which is shown to be mainly due to cancellation of local errors in the integrand of the virial relation for the exchange-energy functional. Utilizing this virial relation a GGA is constructed which reproduces atomic exchange potentials considerably better. This functional does not give as accurately total exchange energies, although it is superior to the second-order gradient expansion. It thus represents a balanced approach aiming at an overall improvement rather than focusing on the exchange energies only. It is concluded that the concept of GGA's due to its simple quasilocal-density dependence is not sufficiently flexible to accurately reproduce exchange potentials and exchange energies simultaneously. It seems that the criteria for judging and constructing approximate exchange functionals put forward in this work and the resulting GGA give a more realistic view of the overall capabilities of GGA's to represent the properties of the true exchange-energy functional, e.g., its functional derivatives, than previous GGA's.

I. INTRODUCTION

In recent years generalized gradient approximations (GGA's) for exchange only[1–8] have been applied to a variety of physical systems. It has been demonstrated that GGA's give excellent atomic ground-state and exchange energies[9,3,10–14] and significantly improve dissociation energies and bond lengths of atomic dimers[9,15,11,12] as well as atomization energies of hydrocarbon molecules.[13] Most notably, however, GGA's are able[16–18] to correct one of the most well-known deficiencies of the local-density approximation (LDA), i.e., its failure to give the correct ferromagnetic bcc ground state for metallic iron.[19,20] Also, the cohesive properties of Al, C, and the semiconductors,[21–23] zinc blende,[24] and the alkali metals[13] are described better by GGA's than the LDA. Energy differences, however, are not consistently improved by GGA's, e.g., ionization potentials and electron affinities are only improved on the LDA in a statistical sense.[13] GGA's (Refs. 25 and 26) do not appreciably help the rather poor LDA (Refs. 27–29) results for *s*-*d* promotion energies. Also, it is not clear whether vibrational frequencies of dimers are improved consistently.[15] As for condensed matter systems, GGA's do not lead to results (in particular for structural properties and the bulk modulus) which are consistently superior to the LDA for a number of solids.[30–32,24,26,33,23] They neither correct the LDA's problems with the transition-metal compounds FeO, CoO, and NiO (Ref. 32) nor the LDA's failure[34] to predict the observed antiferromagnetic ground state for $CaCuO_2$.[35] Also, they reduce the bulk modulus of GaAs, Nb, and Pd too drastically.[23] Consequently, it has been concluded that GGA's are not universally preferable to the LDA (Refs. 30 and 23) as they "do not form a reliable predictive tool with greater precision than the LDA."[33] Furthermore, due to the fact that differences between the results obtained with the various proposed GGA's are often of the order of those between individual GGA's and the LDA, the optimum form of GGA's is not yet clear.[33,23]

Most of these studies examined GGA's for the complete exchange-correlation energy functional $E_{xc}[n]$ and used experimental results for comparison. It is well known, however, that error cancellation between the exchange, $E_x[n]$, and the correlation part, $E_c[n]$, plays an important role in the quality of the combined $E_{xc}[n]$. Moreover, when comparing with experimental data, effects beyond exchange and correlation (such as relativistic contributions or additional approximations required for the numerical treatment of complex systems) can make it difficult to isolate and extract the influence of a specific approximation to $E_{xc}[n]$. In order to understand some of the ambiguities of GGA's for $E_{xc}[n]$ it thus seems necessary to turn to exactly solvable model problems. This is particularly advantageous for the analysis of the exchange-only version of $E_x[n]$.[36,37] Here the so-called optimized-potential model (OPM),[38–41] which represents the definition of the exchange-only, provides an unambiguous standard allowing for detailed microscopic analysis of $E_x[n]$. In particular, the exact OPM exchange potential $v_x(\mathbf{r})$ can be used to judge the quality of the $v_x(\mathbf{r})$'s from any approximate $E_x[n]$ while most previous studies focused on integral quantities such as the exchange energy E_x. Note, however, that it is $v_x(\mathbf{r})$ which determines the spin densities and thus the magnetic phases of solids.

Recently, we have used the information provided by the OPM to discuss the asymptotic properties of GGA's (Ref. 42) and their ability to reproduce spin-dependent quantities[14] such as the spin splitting in the exchange energy, $E_{x\uparrow} - E_{x\downarrow}$, and the exchange potential, $v_{x\uparrow}(r) - v_{x\downarrow}(r)$, of spherical spin-polarized atoms. Both studies exhibited inherent limitations of GGA's. While the basic deficiency of GGA's to reproduce the asymptotic $-1/r$-behavior of $v_{x\sigma}(r)$ for finite systems is not relevant for condensed matter problems, their difficulties with reproducing $v_{x\uparrow}(r) - v_{x\downarrow}(r)$ clearly indicate where wrong predictions of magnetic phases might originate.

In this work we use OPM results for spherical atoms and in particular the corresponding exact $v_{x\sigma}(r)$'s to investigate the local properties of GGAs for exchange-only. For our analysis we have chosen the GGA recently proposed by Perdew and Wang[5] (referred to as PW91 hereafter) which not only satisfies a number of exact relations (e.g., it reduces to the exact lowest-order gradient correction for very small density gradient[43,44]—compare Fig. 2) but also has been specifically constructed to follow closely the GGA of Becke[3] in order to make it reproduce atomic $E_{x\sigma}$'s as well as the latter. By comparing the exact $v_{x\sigma}(r)$ from the OPM with the LDA, PW91, and the second-order gradient expansion (GEA) to $E_x[n_\uparrow, n_\downarrow]$ (Ref. 43) (with the correct prefactor[44,45]) it is shown that PW91 does not reproduce $v_{x\sigma}(r)$ significantly better than the GEA which contrasts with its excellent reproduction of $E_{x\sigma}$'s. Utilizing the virial relation for $E_x[n_\uparrow, n_\downarrow]$,[46,47] it is demonstrated explicitly that the high quality of PW91's $E_{x\sigma}$'s is mainly due to error cancellation. Finally, the virial relation is used to construct a new GGA which reproduces atomic $v_{x\sigma}(r)$'s considerably better than PW91, however, at the price of sacrificing the quality of $E_{x\sigma}$'s to some extent.

It thus becomes clear that GGA's are not able to reproduce both exchange energies and potentials simultaneously with the accuracy indicated by the $E_{x\sigma}$'s of PW91. It is concluded that the concept of GGA's due to its particularly simple form, i.e., its origin in the gradient expansion, does not have sufficient flexibility to include substantially more of the nonlocality in the exact $E_x[n_\uparrow, n_\downarrow]$ than the second-order gradient correction. From this analysis it is not surprising that no unique picture of the quality of GGA's emerges from studies of atoms, dimers, and solids. Our analysis strongly suggests that the expectations resulting from excellent values for $E_{x\sigma}$ produced by some GGA's (Refs. 3 and 5) might have been overly optimistic and that the overall accuracy of the GGA presented in this work characterizes the capabilities of GGA's more realistically.

We use atomic units throughout this paper.

II. REMARKS ON THE CONCEPT OF GGA's

One systematic approach to nonlocal corrections to the LDA is the gradient expansion.[48,43] For the exchange-only $E_x[n_\uparrow, n_\downarrow]$ this expansion reads

$$E_x[n_\uparrow, n_\downarrow] = \sum_{\sigma=\uparrow,\downarrow} \int d^3r\; e_x^{\mathrm{LDA}}(n_\sigma) \times l[1 + c_2\xi_\sigma + c_{41}\xi_\sigma^2 + c_{42}\xi_\sigma\eta_\sigma + c_{43}\eta_\sigma^2 + \cdots], \tag{1}$$

where

$$e_x^{\mathrm{LDA}}(n_\sigma) = -\frac{3k_{F\sigma}(\mathbf{r})}{4\pi}\; n_\sigma(\mathbf{r}), \tag{2}$$

$$k_{F\sigma}(\mathbf{r}) \equiv [6\pi^2 n_\sigma(\mathbf{r})]^{\frac{1}{3}}, \tag{3}$$

$$\xi_\sigma \equiv \left(\frac{\nabla n_\sigma(\mathbf{r})}{2k_{F\sigma}(\mathbf{r})n_\sigma(\mathbf{r})}\right)^2, \tag{4}$$

$$\eta_\sigma \equiv \frac{\nabla^2 n_\sigma(\mathbf{r})}{4k_{F\sigma}^2(\mathbf{r})n_\sigma(\mathbf{r})} \tag{5}$$

and $c_2 = \frac{10}{81}$,[44] $c_{43} = \frac{146}{2025}$,[45] and $c_{41,42}$ are unknown. The general form of GGA's, on the other hand, is given by

$$E_x^{\mathrm{GGA}}[n_\uparrow, n_\downarrow] = \sum_{\sigma=\uparrow,\downarrow} \int d^3r\; e_x^{\mathrm{LDA}}(n_\sigma)\; f(\xi_\sigma) \tag{6}$$

with $f(0) = 1$ and $f(\xi_\sigma)$ is constructed so that the GGA exchange energy does not diverge for exponentially decaying densities. Thus GGA's can be interpreted as an attempt to resum the complete gradient expansion (1). From the comparison of Eqs. (1) and (6) it is most obvious that GGA's are based on two fundamental assumptions: First, although GGA's allow for arbitrarily large density gradients their origin in the conventional gradient expansion makes it quite clear that GGA's can only be expected to be successful for physical systems where ξ_σ is not excessively large (and also higher gradients such as η_σ). In fact, GGA's should work better the smaller ξ_σ becomes. Consequently, GGA's should be most appropriate for metals where ξ_σ is expected to be reasonably small. Second, GGA's represent an attempt to substitute all other ingredients of the gradient expansion such as η_σ in the fourth order by simple powers of ξ_σ. Thus GGA's can only work for systems where this substitution is at least justified to some extent. It is the restriction to the first density gradient, i.e., ξ_σ, as the only nonlocal ingredient which makes the concept of GGA's so appealing for practical calculations and at the same time defines their range of applicability.

The two basic assumptions can be checked for any system under consideration. In Fig. 1 we plot ξ_σ and η_σ for the three spherical atoms Pd, Cr, and Rn which are representative of the 36 atoms we have obtained accurate OPM solutions for (compare a corresponding plot for Kr based on its Hartree-Fock density in Ref. 36). The r dependences of ξ_σ and η_σ clearly reflect the shell structure of the atoms. Although the density is locally decreasing with r even in the interior of atoms, ξ_σ and η_σ remain reasonably small until finally the pure exponential tail of the density for large r leads to an exponential divergence of both ξ_σ and η_σ. Nevertheless, for all but the smallest atoms there is an extended regime of r where $\xi_\sigma < 1$ and which therefore should approximately simulate the situation in solids. Thus although it is not *a priori* clear how small ξ_σ should be to allow for the application of GGA's the first criterion for their applicability seems to be satisfied at least to some extent. Note that the peak and average values of ξ_σ and η_σ decrease with increasing size of the atoms, i.e., with the number of shells present. Thus Rn, the largest atom for which we have obtained an OPM solution, shows the smallest ξ_σ values we have found for atoms. Therefore one should expect Rn to resemble best the situation in metals. Figure 1 also shows that ξ_σ and η_σ in fact have a similar structure in the interior of atoms. But it is equally obvious that η_σ cannot be represented completely by ξ_σ, as η_σ, e.g., becomes negative in various regions of space. Thus the satisfaction of the second basic criterion for the adequacy of GGA's is not clear *a priori.*

To isolate the nonlocal aspects of GGA's it is helpful to define the effective gradient coefficient $g(\xi_\sigma)$ (scaled with respect to c_2),

$$f(\xi_\sigma) \equiv 1 + c_2 g(\xi_\sigma)\xi_\sigma \quad , \tag{7}$$

where

$$g(0) = 1 \tag{8}$$

in order to reproduce the second-order gradient correction for small ξ_σ. For the construction of the kernel $g(\xi_\sigma)$ various schemes have been used. Becke[1,3] and DePristo and Kress[8] have optimized *Ansätze* for $g(\xi_\sigma)$ in order to reproduce atomic exchange energies. Perdew and Wang[4] used a cutoff procedure for the second-order gradient expansion of the exchange hole to enforce certain exact relations for the exchange-energy density. More recently, they combined[5] Becke's *Ansatz*[3] with their concept to satisfy as many exact relations for $E_x[n_\uparrow, n_\downarrow]$ as possible. Vosko and Macdonald, in an attempt to include microscopic information, constructed their $g(\xi_\sigma)$ by fitting the OPM exchange-energy density for a number of atoms.[6] Macdonald and Vosko[7] determined the parameters in their *Ansatz* by minimizing the Hartree-Fock energy resulting from insertion of self-consistent GGA solutions for Xe, a procedure that parallels the OPM energy minimization.

It is important to note one difference between the GGA's of Becke and all others: While Becke does not restrict $g(0)$ all other GGA's satisfy Eq. (8). This restriction certainly should be satisfied in a meaningful way for any GGA to be used for the description of solids. The way in which $g(0) = 1$ is approached, however, is different for the GGA's which satisfy (8). The effective fourth-order coefficient $\bar{c}_{41}$, i.e., the slope of $g(\xi_\sigma)$ for small ξ_σ, varies considerably: While PW91 rises immediately to the $g(\xi_\sigma)$ of Ref. 3 the older GGA's of Refs. 4, 6, and 7 show a somewhat smoother ξ_σ dependence. This is illustrated in Fig. 2, which shows $g(\xi_\sigma)$ for the GGA's of Refs. 3 (B88) and 4 (PW86—using the correct gradient coefficient[49]) as well as PW91. Note that the assumption that $\bar{c}_{41}$ should be of the order of the known coefficient c_{43} would lead to $\bar{c}_{41} \approx 0.6$ ($\approx c_{43}/c_2$) compared to $\bar{c}_{41} = 121$ for PW91 and 6.7 for PW86. While 6.7 is not completely out of the range of $\bar{c}_{41}$ consistent with the concept of

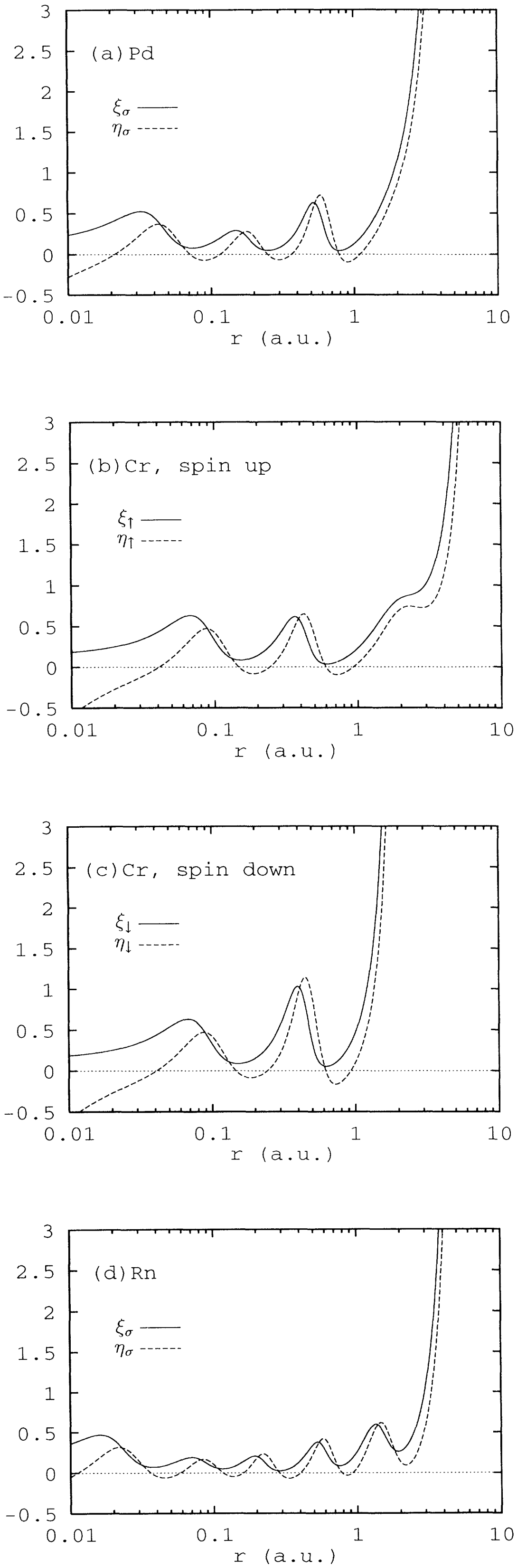

FIG. 1. ξ_σ, Eq. (4), and η_σ, Eq. (5), from OPM solutions for (a) Pd; (b) Cr, spin up; (c) Cr, spin down; and (d) Rn.

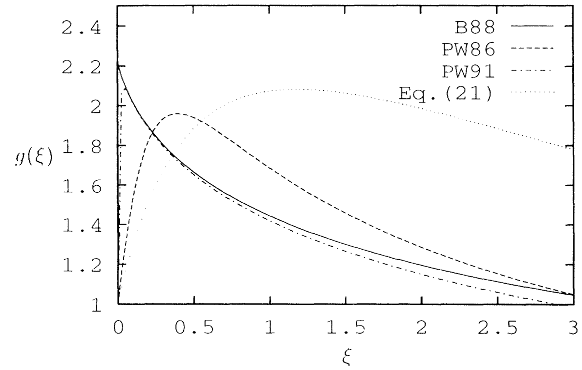

FIG. 2. Effective gradient coefficient $g(\xi_\sigma)$ for the GGA's of Refs. 3 (B88), 4 (PW86), 5 (PW91), and the GGA from the virial relation presented in Sec. IV [Eq. (21)].

gradient expansions, 121 seems to be somewhat excessive. However, there is no rigorous criterion for judging $\bar{c}_{41}$.

The quality of the corresponding atomic exchange energies is shown in Tables I and II where we list the total E_x's for spherical atoms obtained by insertion of OPM densities into the LDA, the second-order gradient expansion[43,44] (GEA) and PW91 together with the corresponding percentage deviations. As is well known the LDA leads to errors ranging from 14% for He to 3.7% for Rn decreasing monotonically with the size of the atoms. The GEA (with the correct gradient coefficient[44]) removes roughly 50–60 % of the LDA's error, for smaller atoms even more. This directly reflects the fact that the correct gradient coefficient is about half as large as the semiempirical coefficients introduced by Herman *et al.*[43] to reproduce atomic exchange energies. PW91, on the other hand, gives excellent exchange energies for almost all these atoms (compare Ref. 13). Note, however, that PW91's error is no longer sign-definite and monotonically decreasing with the size of the systems as for the GEA.

III. ANALYSIS OF THE GGA EXCHANGE POTENTIAL

As already indicated recently[14] the quality of GGA's to reproduce atomic exchange energies is not transferred to the GGA exchange potential,

$$\begin{aligned} v_{x\sigma}^{\mathrm{GGA}}(\mathbf{r}) = v_{x\sigma}^{\mathrm{LDA}}(n_\sigma)\{\ & 1 + c_2 g(\xi_\sigma)[\xi_\sigma - \tfrac{3}{2}\eta_\sigma] \\ & -\tfrac{3}{2}c_2 g'(\xi_\sigma)[\xi_\sigma\eta_\sigma + 2\tau_\sigma] \\ & -\tfrac{3}{2}c_2 g''(\xi_\sigma)\xi_\sigma\tau_\sigma\}, \end{aligned} \qquad (9)$$

where

$$v_{x\sigma}^{\mathrm{LDA}}(n_\sigma) = -\frac{k_{F\sigma}(\mathbf{r})}{\pi}, \qquad (10)$$

$$\tau_\sigma \equiv \frac{\nabla n_\sigma(\mathbf{r}) \cdot \nabla \xi_\sigma(\mathbf{r})}{4k_{F\sigma}^2(\mathbf{r}) n_\sigma(\mathbf{r})}, \qquad (11)$$

and $g'(\xi_\sigma)$ and $g''(\xi_\sigma)$ are the first two derivatives of $g(\xi_\sigma)$, Eq. (7), with respect to ξ_σ. This point is definitively demonstrated in Fig. 3, which shows the nonlocal contributions to $v_{x\sigma}(r)$ from the OPM, the GEA, and PW91, i.e., $[v_{x\sigma}^{\mathrm{OPM,GEA,PW91}}(r) - v_{x\sigma}^{\mathrm{LDA}}(r)]/v_{x\sigma}^{\mathrm{LDA}}(r)$, for Pd, Cr, and Rn. While the GEA removes of the order of 25% of the LDA's error in the interior of the atoms (which should resemble the situation in solids) PW91 does not significantly improve on the GEA. Both the GEA and PW91 cannot follow the exact OPM potential as soon as the asymptotic $-1/r$ behavior begins to set in leading to an upward shift of the shell oscillations. Finally, for large r the $-1/r$ behavior completely dominates $v_{x\sigma}^{\mathrm{OPM}}(r)$ while the GEA diverges and PW91 decays exponentially. Note, that the GEA's capability to remove the LDA's lo-

TABLE I. Total exchange energies $[-E_x = -(E_{x\uparrow} + E_{x\downarrow})]$ of spherical unpolarized atoms for the OPM, LDA, GEA, PW91, and the GGA of Eq. (21) obtained by insertion of OPM densities into Eq. (6) (in hartrees) and the corresponding percentage errors Δ_i.

Atom	OPM	LDA	Δ_{LDA}	GEA	Δ_{GEA}	PW91	Δ_{PW91}	Eq. (21)	$\Delta_{(21)}$
He	1.026	0.884	-13.82	1.007	-1.86	1.017	-0.88	1.076	4.85
Be	2.666	2.312	-13.26	2.581	-3.19	2.645	-0.77	2.792	4.73
Ne	12.105	11.033	-8.85	11.775	-2.73	12.115	0.08	12.382	2.28
Mg	15.988	14.612	-8.61	15.510	-2.99	15.980	-0.06	16.288	1.87
Ar	30.175	27.863	-7.66	29.293	-2.92	30.123	-0.17	30.461	0.95
Ca	35.199	32.591	-7.41	34.183	-2.89	35.165	-0.10	35.513	0.89
Zn	69.619	65.645	-5.71	68.109	-2.17	69.834	0.31	69.968	0.50
Kr	93.833	88.624	-5.55	91.651	-2.33	93.831	0.00	93.800	-0.04
Sr	101.926	96.362	-5.46	99.560	-2.32	101.918	-0.01	101.844	-0.08
Pd	139.114	132.169	-4.99	136.145	-2.13	139.145	0.02	138.833	-0.20
Cd	148.880	141.543	-4.93	145.702	-2.13	148.885	0.00	148.514	-0.25
Xe	179.064	170.566	-4.75	175.304	-2.10	178.991	-0.04	178.374	-0.39
Ba	189.067	180.241	-4.67	185.156	-2.07	189.034	-0.02	188.349	-0.38
Yb	276.147	265.563	-3.83	271.806	-1.57	276.939	0.29	275.532	-0.22
Pt	331.339	318.712	-3.81	325.752	-1.69	331.607	0.08	329.789	-0.47
Hg	345.246	332.143	-3.80	339.372	-1.70	345.427	0.05	343.519	-0.50
Rn	387.453	372.981	-3.74	380.811	-1.71	387.417	-0.01	385.178	-0.59

TABLE II. Total exchange energies $[-E_x = -(E_{x\uparrow} + E_{x\downarrow})]$ of spherical spin-polarized atoms for the OPM, LDA, GEA, PW91, and the GGA of Eq. (21) obtained by insertion of OPM densities into Eq. (6) (in hartrees) and the corresponding percentage errors Δ_i.

Atom	OPM	LDA	Δ_{LDA}	GEA	Δ_{GEA}	PW91	Δ_{PW91}	Eq. (21)	$\Delta_{(21)}$
Li	1.781	1.538	-13.64	1.735	-2.58	1.763	-0.99	1.863	4.62
N	6.604	5.901	-10.65	6.402	-3.07	6.577	-0.42	6.807	3.07
Na	14.013	12.786	-8.76	13.610	-2.88	14.007	-0.04	14.294	2.00
P	22.634	20.793	-8.13	21.956	-3.00	22.596	-0.17	22.934	1.32
K	32.667	30.203	-7.54	31.718	-2.90	32.618	-0.15	32.961	0.90
Cr	47.756	44.646	-6.51	46.600	-2.42	47.839	0.18	48.113	0.75
Mn	50.983	47.674	-6.49	49.704	-2.51	51.036	0.10	51.314	0.65
Cu	65.775	62.007	-5.73	64.387	-2.11	66.025	0.38	66.178	0.61
As	81.496	76.879	-5.67	79.628	-2.29	81.573	0.09	81.637	0.17
Rb	97.870	92.478	-5.51	95.595	-2.33	97.859	-0.01	97.807	-0.07
Mo	119.894	113.652	-5.21	117.250	-2.21	119.902	0.01	119.707	-0.16
Tc	124.377	117.933	-5.18	121.614	-2.22	124.370	-0.01	124.162	-0.17
Ag	144.003	136.854	-4.96	140.926	-2.14	144.011	0.01	143.670	-0.23
Sb	163.811	155.871	-4.85	160.325	-2.13	163.753	-0.04	163.273	-0.33
Cs	184.060	175.393	-4.71	180.223	-2.08	184.001	-0.03	183.350	-0.39
Eu	230.510	220.753	-4.23	226.337	-1.81	230.829	0.14	229.821	-0.30
Re	310.158	298.244	-3.84	304.984	-1.67	310.568	0.13	308.918	-0.40
Au	338.306	325.431	-3.81	332.570	-1.70	338.519	0.06	336.657	-0.49
Bi	366.263	352.442	-3.77	359.978	-1.72	366.302	0.01	364.241	-0.55

cal errors in $v_{x\sigma}(r)$ is smaller than that for reducing the LDA's errors in $E_{x\sigma}$'s. It thus becomes clear that the local quantity $v_{x\sigma}(r)$ is much more difficult to reproduce than the integral quantity $E_{x\sigma}$.

At this point the question arises how GGA's can produce excellent atomic $E_{x\sigma}$'s without really improving the corresponding $v_{x\sigma}(r)$. This question is most directly answered on the basis of the virial relation for exchange only.[46,47] From the definition of the exact exchange-only energy functional,

$$\begin{aligned} E_x[n_\uparrow, n_\downarrow] &= E_{x\uparrow}[n_\uparrow] + E_{x\downarrow}[n_\downarrow] \\ &= \tfrac{1}{2}[E_x[2n_\uparrow] + E_x[2n_\downarrow]], \end{aligned} \tag{12}$$

$$E_{x\sigma}[n_\sigma] = -\frac{1}{2}\int d^3r \int d^3r' \, \frac{\rho_\sigma(\mathbf{r},\mathbf{r}')\rho_\sigma(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}, \tag{13}$$

$$\rho_\sigma(\mathbf{r},\mathbf{r}') = \sum_i \Theta(\epsilon_F - \epsilon_i^\sigma)\, \phi_{i,\sigma}{}^*(\mathbf{r}')\, \phi_{i,\sigma}(\mathbf{r}), \tag{14}$$

$$n_\sigma(\mathbf{r}) = \rho_\sigma(\mathbf{r},\mathbf{r}), \tag{15}$$

where $E_x[n]$ is the exchange-energy functional for unpolarized systems, i.e., $E_x[n_\uparrow, n_\downarrow] = E_x[n_\uparrow + n_\downarrow]$ for $n_\uparrow = n_\downarrow$, and the $\phi_{i,\sigma}(\mathbf{r})$ and ϵ_i^σ are the OPM single-particle orbitals and eigenvalues for given spin σ, it is clear[47] that the basic scaling relation

$$E_{x\sigma}[\lambda^3 n_\sigma(\lambda\mathbf{r})] = \lambda E_{x\sigma}[n_\sigma(\mathbf{r})] \tag{16}$$

holds for either spin. Differentiation with respect to λ then directly leads to

$$E_{x\sigma}[n_\sigma(\mathbf{r})] = \int d^3r \; v_{x\sigma}(\mathbf{r})[3n_\sigma(\mathbf{r}) + \mathbf{r}\cdot\nabla n_\sigma(\mathbf{r})]. \tag{17}$$

Thus the factor $[3n_\sigma(\mathbf{r}) + \mathbf{r}\cdot\nabla n_\sigma(\mathbf{r})]$ is the natural weight connecting $v_{x\sigma}(\mathbf{r})$ and $E_{x\sigma}$.

Equation (17) not only is a very useful tool for checking the accuracy of any calculation[50,14] even for systems where the conventional virial theorem $2T = -V$ does not hold, but also defines an exchange-energy density directly in terms of the unique $v_{x\sigma}(\mathbf{r})$. In Fig. 4 we have plotted the differences between the integrands of Eq. (17) obtained by using $v_{x\sigma}^{\mathrm{LDA}}$, $v_{x\sigma}^{\mathrm{GEA}}$, and $v_{x\sigma}^{\mathrm{PW91}}$ and the exact OPM integrand (using $v_{x\sigma}^{\mathrm{OPM}}$). In all cases PW91 does not remove much of the LDA's local error as is already clear from Fig. 3. It does, however, lead to a much improved balance between regions of positive and negative errors. Thus while the local quality of $v_{x\sigma}^{\mathrm{PW91}}$ is not superior to that of $v_{x\sigma}^{\mathrm{GEA}}$, its subtle error cancellation provides excellent $E_{x\sigma}$'s.

It is worth examining in some more detail which form of $g(\xi_\sigma)$ has the capability to improve on the GEA. To this aim one has to analyze the individual nonlocal terms in $v_{x\sigma}^{\mathrm{GGA}}(r)$, Eq. (9). One first notes that their r dependence is to a large extent determined by the functions multiplying $g(\xi_\sigma)$ and its first two derivatives,

$$u_\sigma(\mathbf{r}) = \xi_\sigma - \tfrac{3}{2}\eta_\sigma, \tag{18}$$

$$v_\sigma(\mathbf{r}) = -\tfrac{3}{2}[\xi_\sigma\eta_\sigma + 2\tau_\sigma], \tag{19}$$

$$w_\sigma(\mathbf{r}) = -\tfrac{3}{2}\xi_\sigma\tau_\sigma \quad , \tag{20}$$

which are essentially independent of the form of $g(\xi_\sigma)$. $g(\xi_\sigma)$ and its derivatives themselves, on the other hand, can only reflect the r dependence of ξ_σ. u_σ, v_σ, and w_σ are plotted in Fig. 5 for Pd, Cr, and Rn. The most important observation from these plots is the fact that u_σ, v_σ, and w_σ are more or less in phase over the complete r regime apart from the asymptotic region. While w_σ is comparably small in the relevant intermediate regime, u_σ and v_σ are of similar size and, apart from fine structure, shape. The $u_\sigma g(\xi_\sigma)$ term in Eq. (9) represents a second-

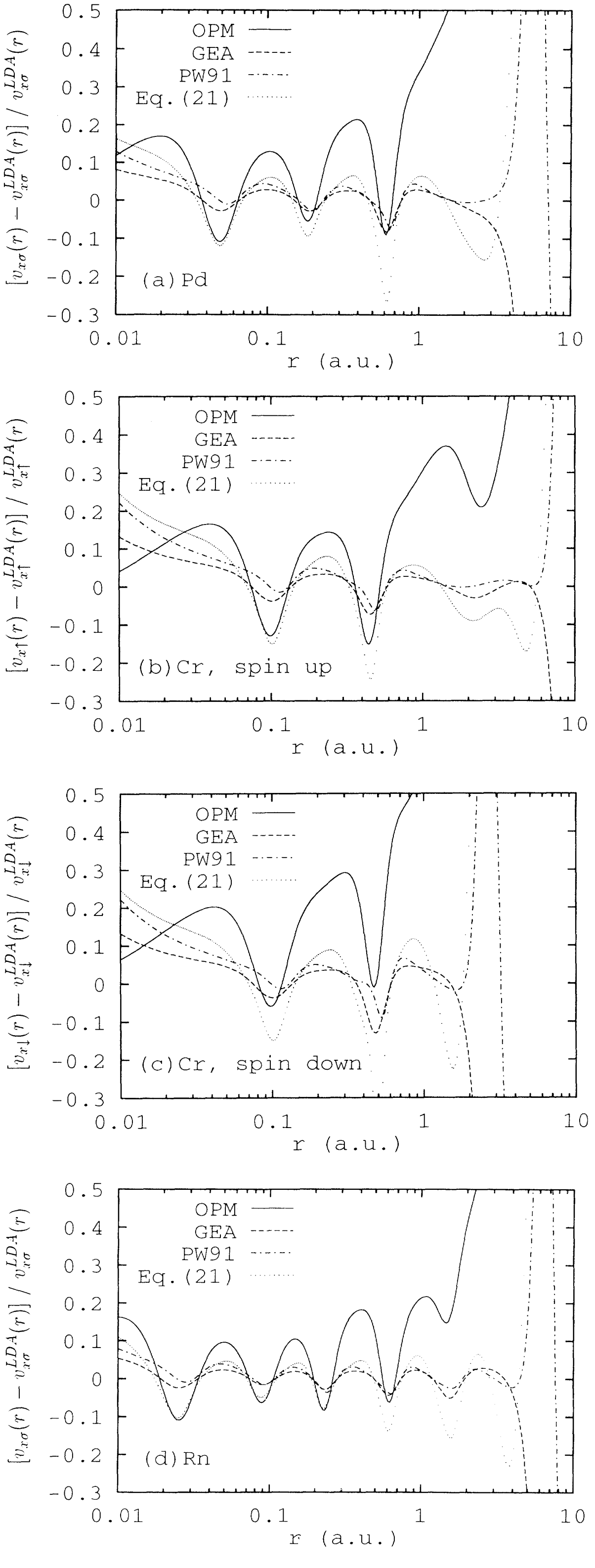

FIG. 3. Nonlocal contributions to the exchange potentials from the OPM, GEA, PW91, and the GGA (21) for (a) Pd; (b) Cr, spin up; (c) Cr, spin down; and (d) Rn. The potentials for the GEA, PW91, and the GGA (21) have been obtained by insertion of exact OPM densities into Eq. (9).

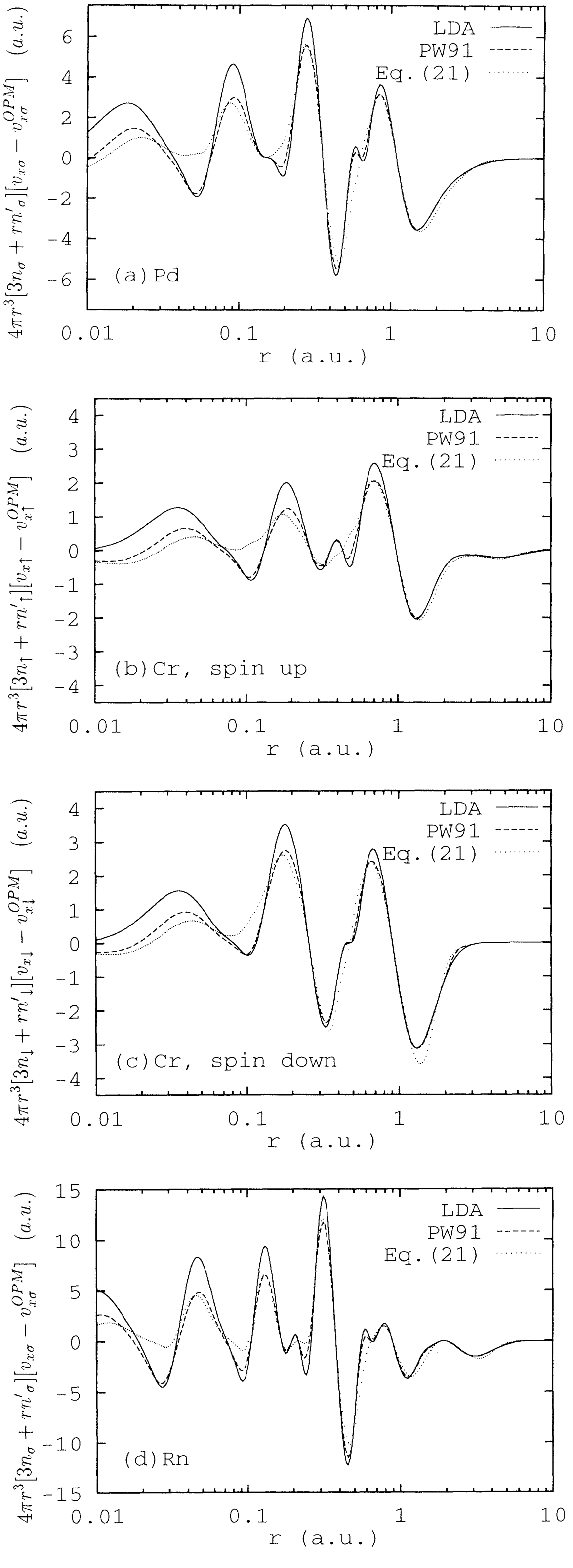

FIG. 4. Differences between the exact OPM integrand in the virial relation (17), $4\pi r^3[3n_\sigma(r) + rn'_\sigma(r)]v_{x\sigma}^{\mathrm{OPM}}(r)$, and the corresponding integrands from the LDA, PW91, and the GGA (21) obtained by insertion of exact OPM densities for (a) Pd; (b) Cr, spin up; (c) Cr, spin down; and (d) Rn.

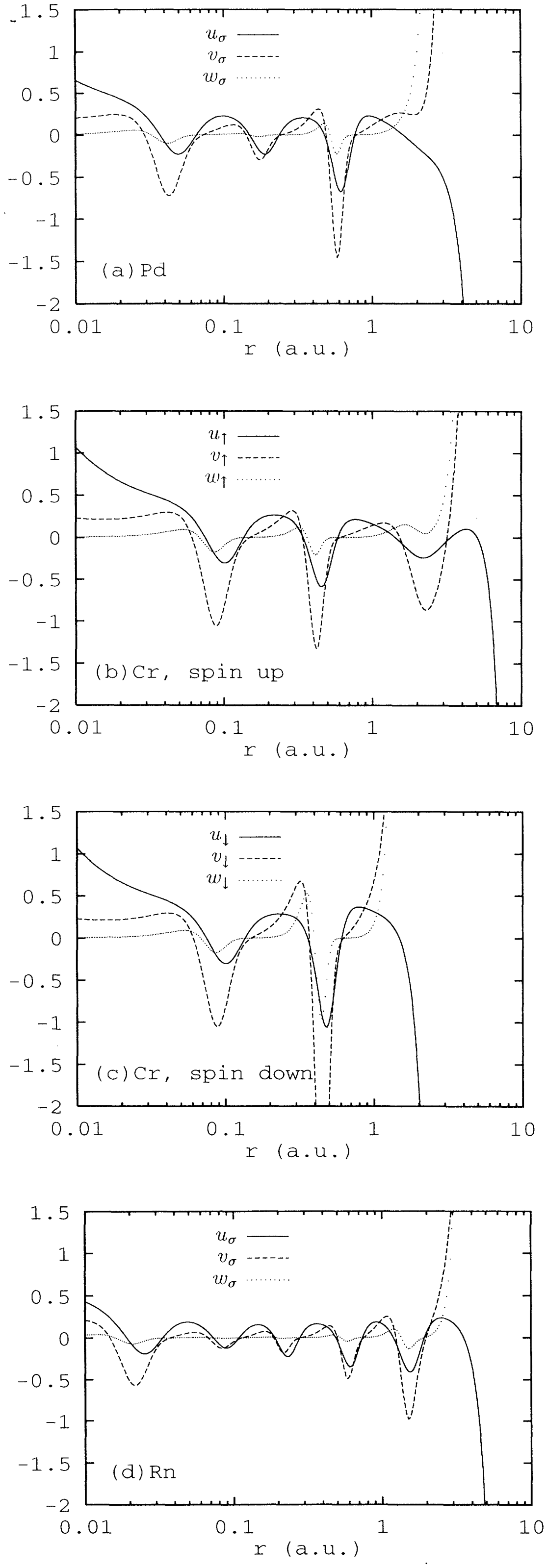

FIG. 5. Individual components u_σ, v_σ, and w_σ, Eqs. (18)–(20), of the nonlocal contribution to $v_{x\sigma}^{\mathrm{GGA}}(r)$, Eq. (9), from OPM solutions for (a) Pd; (b) Cr, spin up; (c) Cr, spin down; and (d) Rn.

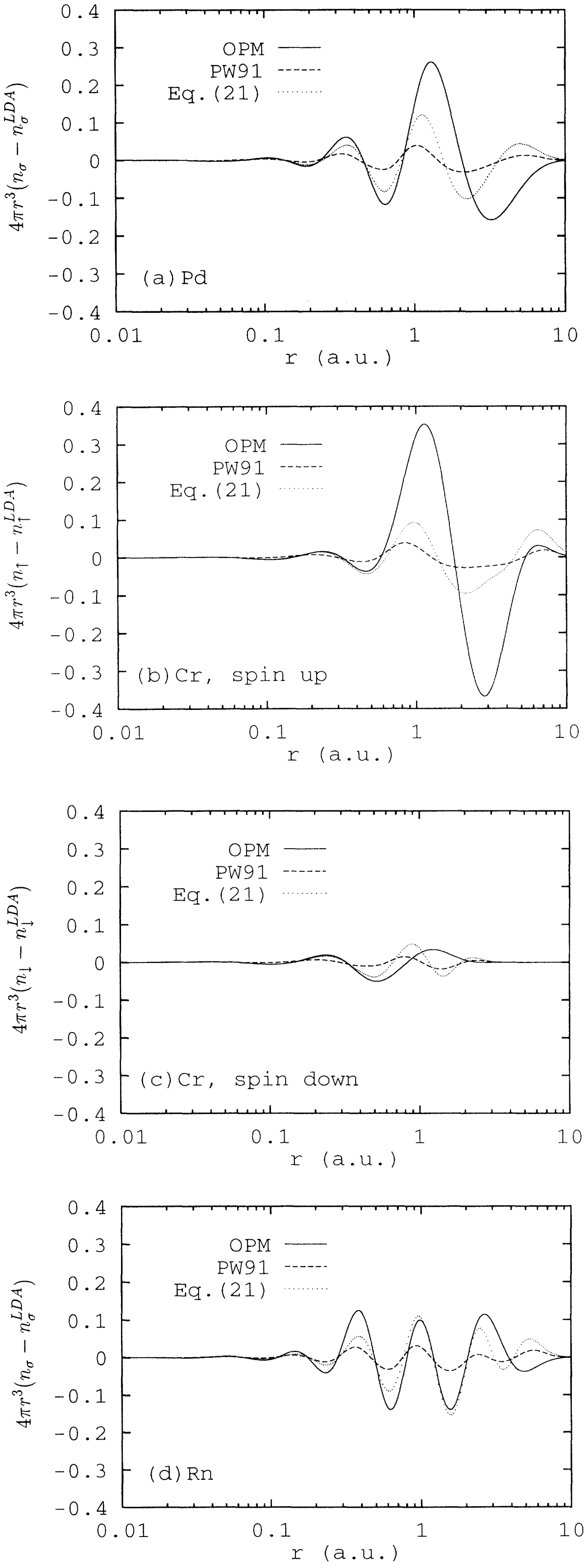

FIG. 6. Differences between exact OPM spin densities and self-consistent spin densities from LDA, PW91, and the GGA (21) and the LDA for (a) Pd; (b) Cr, spin up; (c) Cr, spin down; and (d) Rn.

order gradient correction scaled by the local $g(\xi_\sigma)$. Its potential thus looks like that of the GEA multiplied by the local value of $g(\xi_\sigma)$. Thus to improve on the GEA $g(\xi_\sigma)$ has to be larger than 1 for $0 < \xi_\sigma < 1$: Starting with $g(0) = 1$ the effective gradient coefficient has to rise for small ξ_σ. However, from the fact that the GEA only reproduces about 25% of the oscillations in the nonlocal part of $v_{x\sigma}^{\text{OPM}}(r)$ it is clear that $g(\xi_\sigma)$ would have to rise to a value of 3–4 at $\xi_\sigma \approx 0.5$ in order to reproduce $v_x^{\text{OPM}}(r)$ if there would only be the $u_\sigma g(\xi_\sigma)$ term. In order to obtain a reinforcement of the oscillatory structure from a realistic $g(\xi_\sigma)$ (which should not become much larger than 2) the $v_\sigma g'(\xi_\sigma)$ term must add constructively. This requires $g'(\xi_\sigma)$ to be positive at least for $0 < \xi_\sigma < 0.5$, most likely even up to $\xi_\sigma = 1$. As the $g(\xi_\sigma)$ of PW91 has a negative slope in the relevant ξ_σ regime the two terms add destructively and the resulting $v_{x\sigma}^{\text{PW91}}(r)$ is not much different from $v_{x\sigma}^{\text{GEA}}(r)$.

IV. GGA FROM VIRIAL RELATION

In view of the limited ability of PW91 to reproduce atomic $v_{x\sigma}$'s it is worth examining what the GGA's capability to improve on the GEA in this respect is. In this section the information contained in the OPM exchange potential of spherical atoms is used to construct a GGA which comes significantly closer to the exact $v_{x\sigma}(r)$.

As a kernel of our GGA we use a [3/3]-Padé approximant form

$$f(\xi_\sigma) = \frac{1 + a_1\xi_\sigma + a_2\xi_\sigma^2 + a_3\xi_\sigma^3}{1 + b_1\xi_\sigma + b_2\xi_\sigma^2 + b_3\xi_\sigma^3} \quad , \tag{21}$$

where a_1 and b_1 are restricted to the correct gradient coefficient, $a_1 - b_1 = c_2$. Consequently this *Ansatz* contains five free parameters. To determine these parameters the OPM exchange potentials of 20 spherical atoms are used. In order to make this database approximate the situation in solids as much as possible only rather large atoms are included where ξ_σ is smaller than 1 over an extended range of r values (Kr, Rb, Sr, Mo, Tc, Pd, Ag, Cd, Sb, Xe, Cs, Ba, Eu, Yb, Re, Pt,[51] Au, Hg, Bi, Rn). Note that a [2/2]-Padé function gives almost identical results indicating that the form (21) has sufficient variational freedom.

In order to utilize the exact OPM exchange potential on a point by point basis for determining free parameters (or more complex ingredients) of any given *Ansatz* for $E_x[n_\uparrow, n_\downarrow]$ one needs a quality criterion based on $v_{x\sigma}(r)$. The most natural criterion we found is the local reproduction of the integrand of the virial relation (17),

$$\sum_{\sigma=\uparrow,\downarrow} \sum_{k=1}^{20} \frac{4\pi}{E_{x\sigma,k}} \int_0^\infty r^2 dr |[3n_{\sigma,k}^{\text{OPM}}(r) + rn'^{\text{OPM}}_{\sigma,k}(r)]\{v_{x\sigma,k}^{\text{OPM}}(r) - v_{x\sigma}^{\text{GGA}}[n_{\sigma,k}^{\text{OPM}}; r]\}| \quad , \tag{22}$$

where $n'_\sigma(r)$ is the first derivative of $n_\sigma(r)$ with respect to r. As the virial relation directly connects $v_{x\sigma}(r)$ with the resulting total $E_{x\sigma}$ a kernel $f(\xi_\sigma)$ which approximates the OPM integrand reasonably well should not only be expected to give improved $v_{x\sigma}(r)$'s but also good $E_{x\sigma}$'s. Minimizing this local deviation from the virial exchange energy density, we obtained $a_1 = 1.647\,127$, $a_2 = 0.980\,118$, $a_3 = 0.017\,399$, $b_1 = 1.523\,671$, $b_2 = 0.367\,229$, $b_3 = 0.011\,282$. The corresponding $g(\xi_\sigma)$ is plotted in Fig. 2. As is obvious from the comparison to PW91 and the older GGA of Perdew and Wang (PW86) the GGA based on the OPM exchange potential is quite different from the former GGA's. It has a smaller effective fourth-order coefficient $\bar{c}_{41} = 3.4$ thus coming closer to the estimate from the straight gradient expansion. Also, $g'(\xi_\sigma)$ stays positive over a larger regime of ξ_σ for this GGA which was to be expected from the discussion in Sec. III. Note that our database is dominated by regions of r where $\xi_\sigma \leq 1$. While this should simulate the situation in solids reasonably well it does not really fix $g(\xi_\sigma)$ for ξ_σ values much larger than 1. This is, however, no serious restriction since one can not expect GGA's to work in this regime and $\xi_\sigma >> 1$ should not occur in solids for which GGA's are primarily constructed.

The exchange potentials resulting from this GGA are given in Fig. 3. It is most obvious that this GGA makes a considerable effort to follow the oscillations in the nonlocal part of the exact $v_{x\sigma}$. In particular in the interior of the most characteristic large atoms [compare Rn, Fig. 3(d)] it is closer to $v_{x\sigma}^{\text{OPM}}(r)$ than all other GGA's we have considered. Due to the restricted form of GGA's (Ref. 42) it is not able to follow the asymptotic $-1/r$ behavior of the exact $v_{x\sigma}^{\text{OPM}}(r)$ and as a consequence it also does not reproduce the remnant of this asymptotic form, i.e., the upward shift in the oscillations which develops already in the intermediate r regime. Note that this upward shift is not just given by some smooth function of r but rather shows some structure itself. However, one would not expect such a large shift to be present in the $v_{x\sigma}^{\text{OPM}}(r)$ of solids.

The improved quality of the exchange potential resulting from the GGA (21) is transferred to the corresponding self-consistent densities: They reproduce the exact densities better than those from PW91 as can be seen from Fig. 6 (where again the LDA is used as the standard). A further measure for the quality of the orbitals resulting from self-consistent calculations are the ground-state energies obtained by insertion of the self-consistent solutions into the exact exchange-only energy functional, i.e., the Hartree-Fock energy expression. The corresponding values are given in Tables III and IV. For all but the smallest atoms the GGA (21) leads to significantly lower ground-state energies. In fact, the improvement of the GGA (21) on PW91 is as large as the improvement PW91 makes with respect to the LDA.

Comparing the total E_x's from the GGA (21) with the GEA and PW91 (see Tables I and II) one recognizes a fundamental limitation of GGA's: The price of improv-

TABLE III. Total OPM ground-state energies ($-E_{\rm tot}^{\rm OPM}$) of spherical unpolarized atoms and deviations of ground-state energies obtained by insertion of self-consistent solutions using the LDA, PW91, and the GGA of Eq. (21) into the exact total-energy functional from $-E_{\rm tot}^{\rm OPM}$ (in hartrees).

Atom	$-E_{\rm tot}^{\rm OPM}$	$E_{\rm tot}^{\rm OPM} - E_{\rm tot}^{\rm LDA}$	$E_{\rm tot}^{\rm OPM} - E_{\rm tot}^{\rm PW91}$	$E_{\rm tot}^{\rm OPM} - E_{\rm tot}^{\rm Eq.\ (21)}$
He	2.862	-0.004	-0.003	-0.004
Be	14.572	-0.004	-0.003	-0.004
Ne	128.545	-0.018	-0.015	-0.014
Mg	199.612	-0.014	-0.010	-0.005
Ar	526.812	-0.017	-0.011	-0.006
Ca	676.752	-0.016	-0.009	-0.003
Zn	1777.834	-0.051	-0.039	-0.025
Kr	2752.043	-0.032	-0.021	-0.010
Sr	3131.534	-0.029	-0.017	-0.006
Pd	4937.906	-0.049	-0.035	-0.024
Cd	5465.115	-0.044	-0.027	-0.009
Xe	7232.121	-0.034	-0.018	-0.007
Ba	7883.527	-0.033	-0.016	-0.004
Yb	13391.417	-0.080	-0.062	-0.049
Pt	17331.093	-0.068	-0.049	-0.034
Hg	18408.961	-0.062	-0.040	-0.019
Rn	21866.746	-0.048	-0.028	-0.015

ing $v_{x\sigma}(r)$ is a loss of quality for $E_{x\sigma}$. It is important to note, however, that for the relevant large atoms the GGA (21) still leads to much better $E_{x\sigma}$'s than the GEA. From Fig. 4 one can see that as a consequence of its superior $v_{x\sigma}(r)$ the GGA (21) comes closer to the exact virial integrand than PW91. It does, however, not achieve the same degree of error cancellation as PW91. It thus represents a GGA which tries to make a balanced improvement for both integral quantities like $E_{x\sigma}$ and local quantities like $v_{x\sigma}(r)$. One would hope that this GGA leads to a more systematic improvement on the LDA than previous GGA's.

It is clear from the discussion in Sec. III and the preceding paragraphs that the rather simple functional form of GGA's does not allow a simultaneous highly accurate reproduction of both $E_{x\sigma}$'s and $v_{x\sigma}(r)$'s. Thus the extreme accuracy for $E_{x\sigma}$'s which PW91 and the GGA's of Refs. 3 and 42 does not reflect the actual predictive

TABLE IV. Total OPM ground-state energies ($-E_{\rm tot}^{\rm OPM}$) of spherical spin-polarized atoms and deviations of ground-state energies obtained by insertion of self-consistent solutions using the LDA, PW91, and the GGA of Eq. (21) into the exact total-energy functional from $-E_{\rm tot}^{\rm OPM}$ (in hartrees).

Atom	$-E_{\rm tot}^{\rm OPM}$	$E_{\rm tot}^{\rm OPM} - E_{\rm tot}^{\rm LDA}$	$E_{\rm tot}^{\rm OPM} - E_{\rm tot}^{\rm PW91}$	$E_{\rm tot}^{\rm OPM} - E_{\rm tot}^{\rm Eq.\ (21)}$
Li	7.433	-0.004	-0.002	-0.004
N	54.403	-0.010	-0.007	-0.007
Na	161.857	-0.015	-0.011	-0.008
P	340.715	-0.015	-0.009	-0.005
K	599.159	-0.016	-0.009	-0.004
Cr	1043.346	-0.037	-0.027	-0.020
Mn	1149.860	-0.034	-0.024	-0.014
Cu	1638.952	-0.056	-0.047	-0.039
As	2234.228	-0.037	-0.025	-0.012
Rb	2938.346	-0.030	-0.018	-0.007
Mo	3975.537	-0.037	-0.023	-0.010
Tc	4204.779	-0.037	-0.022	-0.007
Ag	5197.682	-0.047	-0.031	-0.015
Sb	6313.470	-0.037	-0.020	-0.006
Cs	7553.917	-0.033	-0.017	-0.005
Eu	10423.524	-0.061	-0.043	-0.030
Re	15784.513	-0.064	-0.044	-0.027
Au	17865.371	-0.065	-0.044	-0.026
Bi	20095.561	-0.053	-0.031	-0.015

power of these GGA's which to a large extent is determined by their much more limited ability to reproduce local quantities.

V. CONCLUDING REMARKS

In this paper we have shown that the accuracy with which one of the most recent GGA's (Ref. 5) for exchange-only reproduces atomic exchange energies is not present in its corresponding exchange potentials. In fact, this GGA does not improve on the second-order gradient expansion in the regime of small density gradients. The virial relation demonstrates that its accuracy for exchange energies is mostly due to cancellation of local errors. In an effort to reduce such local errors, the virial relation[46,47] has been used to construct a GGA which leads to much better exchange potentials. The corresponding atomic exchange energies, however, are not as accurate as those of Ref. 5. Still, they represent a definite improvement over the second-order gradient approximation.

The accuracy of the atomic $E_{x\sigma}$'s from some GGA's might have led to overly optimistic expectations (see, e.g., Ref. 8) for the general capabilities of GGA's. The concept of GGA's due to their very simple quasilocal-density dependence should not be expected to be so much superior to the gradient expansion from which it originates. In this respect the GGA put forward in this work might characterize the true overall improvement GGA's represent more realistically. For large atoms it reduces the GEA's errors in exchange energies by almost a factor of 3. While the corresponding improvement of $v_{x\sigma}(r)$ is not as easily summarized, an average error reduction of about 50% might indicate its quality in this respect. Although, given the limitations of GGA's, functionals focusing on total exchange energies might be useful in certain applications, it seems that a balanced GGA like the one presented in this work should in general be preferable.

In conclusion we would like to stress that from all our comparisons of the LDA and GGA's with exact OPM results it is clear that GGA's for exchange-only represent an improvement on the LDA. Lacking any easily implementable alternative to GGA's it seems appropriate to use them having in mind that due to their limited capabilities as demonstrated in this and recent papers[42,14] they will solve some but not all problems one has faced with the LDA.

As is clear from Sec. IV the GGA (21) has not been constructed in combination with a counterpart for correlation but rather as an optimum GGA for exchange-only. Due to the fact that the most commonly used GGA's for correlation[37,52,53,5] have been developped in conjunction with specific approximations to $E_x[n_\uparrow, n_\downarrow]$ and that error cancellation plays an important role for the combined $E_{xc}[n_\uparrow, n_\downarrow]$ it seems preferable at this point to use the GGA (21) with the LDA for correlation.

Finally we want to emphasize the general applicability of the virial relation as a tool for testing and constructing approximate $E_x[n_\uparrow, n_\downarrow]$. It is most suitable for examining to what extent the quality of integral quantities is also present in local quantities. While in this work the virial relation has been used to discuss the local properties of GGA's it can be utilized for any other approximate $E_x[n_\uparrow, n_\downarrow]$ independently of the degree of nonlocality.

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