

Regularized Gradient Expansion for Atoms, Molecules, and Solids

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Abstract: A new, regularized gradient expansion (RGE) approximation density functional (i.e., a generalized gradient approximation or GGA that recovers the second-order gradient expansion for exchange in the slowly varying limit) was designed in an attempt to obtain good solid-state and molecular properties at the same time from a single GGA. We assess the performance of this functional for molecular atomization energies, solid lattice constants, and jellium surface energies. We compare the performance of this functional to the modified Perdew-Burke-Ernzerhof generalized gradient approximation (PBEsol GGA), the original PBE GGA, and the Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA.

1. Introduction

Kohn–Sham spin density functional theory^{1,2} is now the most widely used method to calculate the ground-state energies of atoms, molecules, solids, surfaces, and more complex systems. In Kohn–Sham theory, the exchange–correlation energy is a functional of the electron spin densities and is the only quantity that must be approximated. The development of increasingly accurate but universal approximations, for use throughout condensed matter physics and quantum chemistry, is the aim of this work. This development relies upon physical insights, paradigm examples, and exact constraints on the exchange–correlation energy, plus minimal empiricism where necessary.

The popular density functionals can be assigned to the rungs of a Jacob’s ladder³ according to their number and kind of ingredients. The local ingredients include the electron density, the gradient and Laplacian of the density, and other quantities that are indirectly determined by the density, constructed from the Kohn–Sham orbitals. The more sophisticated density functionals^{4–7} include the kinetic energy density as well. Climbing up to the ladder, the

accuracy of the density functionals increases, and the high-level approximations are expected to achieve the goal of functional development: to achieve high accuracy for a wide range of systems from solids to atoms.

The lowest rung of the ladder, the LSDA (local spin density approximation),¹ uses the electron density only, is exact for the uniform electron gas, and reaches moderate accuracy for systems with slowly varying density. The nonempirical GGA (generalized gradient approximation)⁸ density functionals rely on the correct features of the LSDA while improving the atomization energies which are seriously overestimated by the LSDA. Although some semiempirical GGAs are more accurate for molecules, they all fail to provide good lattice constants and surface energies. The generally useful nonempirical PBE-GGA⁹ satisfies two constraints relevant to solids, the uniform-density limit and the good linear response of the LSDA.

It was shown in ref 10 that the exchange energy of neutral atoms is well approximated by an asymmetric expansion in the atomic number Z : $E_x = -2.208Z^{5/3} - 0.196Z + \dots$ The first term is determined by the LSDA, while the second term arises from the gradient expansion of a GGA approximation. In order to be asymptotically exact for large Z , and accurate for most finite Z , the functional must account for both the slowly varying term and the cusp correction. No GGA can get both effects right individually. The exchange gradient

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expansion coefficient (μ) of the popular GGAs was set to obtain good atomic and atomization energies and good thermochemistry. This coefficient, however, is about twice as large as the exact slowly varying gradient expansion coefficient for exchange ($\mu_{\text{GGA}} = 0.22\text{--}25$ vs $\mu_{\text{GEA}} = 10/81$).

Results for molecular atomization energies support the conclusion that PBE is a generally useful nonempirical GGA. The PBE form satisfies two constraints for solids, and thus it can be a reasonable starting point for further development. Unfortunately, the surface energy of jellium in the PBE approximation is less accurate than that of LSDA.¹¹

On the other hand, the GGA is a very limited functional form that must necessarily be somewhat biased toward either atoms and small molecules or toward solids and surfaces. The derivation of the PBE GGA by constraint satisfaction⁹ had to choose two out of three constraints on the small-gradient behavior, since a single GGA cannot satisfy all three together. And it had to choose a particular way of satisfying these constraints. These choices were influenced by the prior GGA construction from the sharp real-space cutoff of the spurious long-range parts of the gradient expansions⁸ for the exchange and correlation hole densities. The employed sharp or step-function cutoffs are parameter-free but are more appropriate to atoms and small molecules (where the electron density cuts off exponentially) than to solids (where the holes can be more diffuse).

Reference 10 concluded that while the second-order gradient expansion is relevant to solids, those real systems are much closer to the limit of validity of the expansion for exchange than they are for correlation. If we are interested only in solids, it makes more sense to use the first principles gradient coefficient for exchange $\mu=0.123$ and choose $\beta=0.037$ to recover the good LSDA linear response. Greater accuracy requires us to make a fission and led us recently to develop the successful PBEsol¹² for solids while keeping the successful PBE for atoms.

By incorporating more complex ingredients and exact properties into the exchange-correlation energy, a higher-rung functional can simultaneously recover the good LSD linear response and the correct second-order gradient expansion for both exchange and correlation. Meta-GGAs improve upon the GGAs by the satisfaction of one paradigm for condensed matter and another for quantum chemistry. The paradigm for condensed matter physics is the slowly varying limit,¹³ and that for quantum chemistry is the one and two-electron density.¹⁴ The kinetic energy density is an ingredient which permits recovery of the slowly varying limit through higher-orders in the ∇ operator.

Since meta-GGAs are not widely available in solid state codes, there has been a great need to develop simple low-level functionals that are accurate for restricted classes of systems (e.g., solids). The semilocal functionals of the first three rungs are computationally efficient in self-consistent calculations.

Predicting lattice constants more accurately than LSDA remains a challenge, even for state-of-the-art meta-GGAs; the TPSS meta-GGA only achieves a moderate improvement upon the Perdew-Burke-Ernzerhof (PBE) GGA.¹⁵ We built

the correct physics for solids into the new PBEsol generalized gradient approximation,¹² and we have cast it in a form that makes it extremely easy for solid-state calculators to test and apply. On the other hand the PBE is more successful in chemistry than PBEsol, because it more radically reduces the LSD overestimate of molecular atomization energies. This situation motivated us to try to develop GGAs without being biased toward either atoms and small molecules on the one hand or toward solids and surfaces on the other, combining all the favorable properties of different GGAs. For recent developments building on the PBEsol concept see ref 16.

II. Regularized Gradient Expansion

A universally useful GGA is approached in this work by adding a higher-order term to the denominator of the PBEsol GGA enhancement factor. We recall the exchange enhancement factor $F_x^{\text{PBE}(s)}$ for PBE GGA, which gives the enhancement over LSDA exchange as a function of the reduced density gradient s (defined below). The parameter μ controls the approach of F_x^{PBE} to its slowly varying or $s \rightarrow 0$ and rapidly varying or $s \rightarrow \infty$ limits (1 and $1 + \kappa$, respectively), while the parameter $\kappa = 0.804$ sets the large-gradient limit. (Satisfaction of the Lieb-Oxford bound¹⁷ on E_x for all possible densities requires $\kappa \leq 0.804$, and $\kappa = 0$ recovers LSDA exchange.)

PBEsol is a first (RGE1) regularized gradient expansion (RGE) approximation, because it removes the spurious divergence of the second-order gradient expansion. A second RGE or RGE2 exchange energy also has the form

$$E_x^{\text{RGE2}}[n] = \int d^3r n \epsilon_x^{\text{unif}}(n) F_x^{\text{RGE2}}(s) \quad (1)$$

where $\epsilon_x^{\text{unif}}(n) = -3(3\pi^2 n)^{1/3}/4\pi$ is the exchange energy per electron for the uniform electron gas of density n , and $s = |\nabla n|/[4(3\pi^2 n)^{1/3}n]$ is the dimensionless density gradient. The form of eq 1 satisfies the uniform density scaling property of the exchange energy.

For the second-order gradient coefficient for exchange, valid for the slowly varying limit, we use the first-principles $\mu = 10/81$ as justified in ref 12

$$F_x^{\text{RGE2}}(s) = 1 + \kappa - \frac{\kappa}{1 + \frac{\mu s^2}{\kappa} + \left(\frac{\mu s^2}{\kappa}\right)^2} \quad (2)$$

Note that $F_x(s) = 1 + \mu s^2 + \dots$ as $s \rightarrow 0$ and that the s^4 term of this expansion is designed to vanish for RGE2. In other words, RGE2 is designed to recover the second-order gradient expansion for exchange over a wide range of s . In the large-gradient limit

$$\lim_{s \rightarrow \infty} F_x \rightarrow 1 + \kappa \quad (3)$$

In this work we restore the slowly varying limit over a wide range of s . This choice can give more accurate lattice constants and surface energies than PBE.¹² But with the successful PBEsol functional for solids we encountered a dilemma: no functional achieved high accuracy for solid

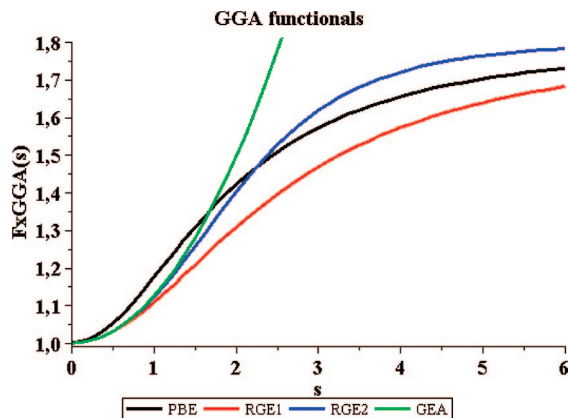


Figure 1. Comparison of the PBE, RGE1 (PBESol), RGE2, and GEA ($1 + 10/81 s^2$) exchange enhancement factors for reduced exchange gradient s ($0 \leq s \leq 6$).

properties and atomic energies at the same time. With the selection of $\mu = 10/81$ we cannot ensure good quality atomization energies within the limited frame of the PBESol GGA, since GGAs cannot use other inputs than the electron density and its gradient. At the higher meta-GGA level, the parameter μ is determined by recovering the PBE-GGA large gradient limit, and the functional can be exact to fourth-order in the slowly varying limit. We miss this flexibility at the GGA level and have to find a reasonable interpolation between the large gradient and small gradient limits. In other words we have to find the way to resolve this inconsistency of the GGAs without climbing up to the meta-GGA level.

With this formulation of the denominator of F_x in the RGE2, we try to restore the approach of F_x to the large gradient limit at the GGA level, keeping μ at its exact value justified in the successful PBESol functional. This form gives better atomic exchange energies than the PBESol (RGE1) form. The RGE1 functional is defined as PBESol exchange combined with the standard PBE correlation. Our RGE2 formula satisfies the Lieb-Oxford bound like PBE,⁹ and, since the spin-polarized F_x increases with s to a maximum value of $F_x \leq 1.804$, the Lieb-Oxford bound is satisfied as well.

The nonlocality of F_x is displayed in Figure 1, where we also compare F_x of the RGE2 and RGE1 (PBESol) functionals over the range of interest for real systems. The range $0 \leq s \leq 3$ is the important region for most properties of real systems, while $0 \leq s \leq 1$ is relevant for the valence-electron regions of densely packed solids. For a universally useful functional, the nonlocality must be enhanced for $s \geq 2$, compared to the RGE1 functional. The approach of F_x to the large-gradient limit seems to be relevant for free atoms.¹² The RGE2 F_x agrees well with the RGE1 in the valence region of densely packed solids and increases over the PBE-GGA in the relevant large gradient region for the free atoms.

The increase with s has been discussed in the context of the atomization energies.¹⁸ Other works on atomization energies and isodesmic stabilization energies¹⁹ confirm that real systems can be split into two groups: solids and molecules.²⁰ These groups represent two different universality classes for the gradient expansion; in the solids the electrons live in the classically allowed region, while in the

molecules they spend considerable time in classically forbidden regions.

Our universally useful RGE2 is expected to respect both classes, and in addition an earlier work by us¹⁹ confirmed that the diminished gradient makes the semilocal functionals better not only for solids but also for single-bonded hydrocarbons.

It has been known for a long time that the PBE-GGA overestimates the atomization energies. This overbinding is attributed to an inconsistency of the atomic and molecular energies at the GGA level of approximation.¹⁸ The overestimation is increased with the reduced gradient expansion PBESol and arises from the worsened total energies of the free atoms. The RGE2 is expected to improve the bad-quality atomization energies of the PBESol GGA due to increased F_x values in the large- s region. Accurate total energies of free atoms call for an increased F_x in the region of $s \geq 2$ relevant to free atoms, although an overenhanced exchange might spoil the energies of molecules leading to overestimation of atomization energies.

For a slowly varying density, the correlation energy has a second-order gradient expansion

$$E_c[n] = \int dr^3 n [\epsilon_c^{unif}(n) + \beta t^2] \quad (4)$$

where

$$t = \frac{|\nabla n|}{[2\sqrt{4(3\pi^2 n)^{1/3}/\pi}]n} \quad (5)$$

is the reduced correlation gradient on the scale of the Thomas-Fermi screening wave vector instead of the Fermi wave vector used in the exchange. The value of the correlation gradient expansion coefficient β respects the expansion from the work of Langreth and Perdew, which implies the Ma-Brueckner high-density limit for the gradient coefficient for correlation.^{21,22}

Once again, as in our PBESol work, the role of correlation should be revisited. Since the convergence conditions are more severe for the second-order gradient expansion in the case of correlation than they are in the case of exchange, it may not be so important in practice to recover the correct Langreth-Vosko gradient expansion for correlation, even in solids.²³

Another condition relevant to solids is the linear response of the uniform electron gas to a weak perturbing potential. For small density variations of the uniform gas, the LSD is an accurate approximation, while the second-order gradient expansion is not. For such small density variations, s and t will be small, and a GGA will have the expansions (1) and (4). A good description which recovers the LSD requires a cancelation between the second-order gradient terms

$$\mu = \frac{\pi^2}{3} \beta \quad (6)$$

We have shown in the PBESol construction that the GGA form is too limited to allow for a perfect description of all small density variations, so a choice must be made among the constraints. We can keep the original PBE form but

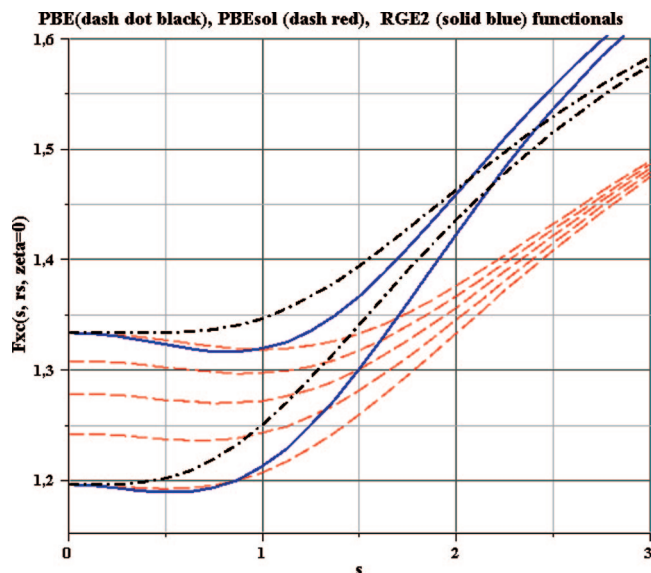


Figure 2. Exchange-correlation gradient enhancement factors, $F_{xc}(s, r_s, \zeta=0)$ vs the reduced density gradient s in the range $0 \leq s \leq 3$ for the generalized gradient approximations PBE (dash dot black), PBEsol (dash red), and RGE2 (solid blue) for $r_s = 2, 3, 4, 5$, and 6 (PBEsol) and $r_s = 2$, and 6 (PBE and RGE2). r_s denotes the Wigner-Seitz radius, and ζ denotes the relative spin polarization. $r_s = 2$ and 6 are the smallest and largest enhancement factor curves, respectively. In LDA $F_{xc}(s, r_s, \zeta=0) = F_{xc}(s=0, r_s, \zeta=0)$.

change the second-order gradient coefficients for exchange and correlation to satisfy solidlike constraints. The expansion of the correlation has proven to be less relevant, and eq 6 can be respected by a reduced gradient coefficient for correlation. With this choice we could keep the constraint of the linear response in our RGE2 as well, but we decided to follow the way we chose for the PBEsol functional and sacrifice the constraint of the linear response for the sake of good surface energies. The correlation gradient expansion coefficient $\beta = 0.053$ of the RGE2 correlation was set to obtain TPSS jellium surface exchange-correlation energies in the same way as in PBEsol (see discussion later). Figure 2 shows the comparison between the PBE, PBEsol, and RGE2 exchange-correlation enhancement factors $F_{xc}(s, r_s, \zeta = 0)$ for the spin-unpolarized density, where r_s is the Wigner-Seitz radius and $\zeta = (n_\uparrow - n_\downarrow)/n$ is the relative spin polarization (here $\zeta = 0$) and

$$E_{xc}^{RGE2}[n] = \int d^3r n \epsilon_x^{unif}(n) F_{xc}^{RGE2}(s, r_s, \zeta) \quad (7)$$

For small s , the PBEsol and RGE2 functionals are quite similar for electron densities around $2 < r_s < 6$ (typical for valence region of the metals studied in this paper). However, for large s values, the two functionals behave quite differently, as shown in Figure 2.

The exchange-correlation (xc) energy E_{xc}^{hybrid} of the hybrid functionals is defined as

$$E_{xc}^{hybrid} = a E_x^{HF} + (1 - a) E_x^{DFA} + E_c^{DFA} \quad (8)$$

where a is a mixing factor of E_x^{HF} Hartree–Fock, and E_x^{DFA} density functional approximation (local GGA or meta-GGA

functionals) exchange energies, and E_c^{DFA} is a density functional approximation correlation energy. The value of a cannot be fixed universally. Good thermochemistry can be obtained by setting $0.1 < a < 0.25$ (cf. PBEh and TPSSH in Table 1). To obtain good reaction energy barriers usually $a > 0.5$ values are required. The amount of HF exchange was controlled via Iop(3/76) of the GAUSSIAN program.³⁰

III. Results and Discussion

In an assessment of a universal density functional, the performance has to be tested on a test of atomization energies and bulk solids. We used a triple- ζ -quality basis set. The AE6 test set of Lynch and Truhlar²⁴ provides a quick but representative evaluation for the atomization energies of diverse molecular systems: the AE6 set of atomization energies includes six molecules: SiH₄, S₂, SiO, C₃H₄, C₂H₂O, and C₄H₈.

This test set is small, however quite diverse, and was constructed to reproduce the error of larger sets. For the AE6 data set, we show two sets of results coming from different correlation parameters β of eq 4. $\beta = 0.066725$ reproduces the original PBE correlation, while the selection of $\beta = 0.053$ sacrifices the good linear response in favor of better surface energies (*vide infra*) and comes from a fitting to meta-GGA (TPSS) quality surface energies.

The results in Table 1 show that the value of the parameter β influences the results, and $\beta = 0.066725$ gives better agreement with experiment. Both version of the RGE2/6–311G(3df,2p) improve the atomization energies considerably compared to the PBEsol/6–311G(3df,2p) results. This shows clearly the importance of the larger enhancement factor F_x for the large gradient limit for better atomization energy. For functionals that show overbinding tendency, like PBE, PBEsol, and RGE2, applying a smaller basis set (e.g., 6–311G(d,p)) improves the agreement with the experimental results, as shown in ref 18. We constructed hybrids from the PBEsol and RGE2 functionals, denoted as PBEsolh and RGE2h in Table 1 (cf. eq 8). To obtain best agreement with experiment for the AE6 test set, we mix 37% exact exchange with the RGE2 GGA exchange. This gives almost as good a result as that of the quite good TPSSH functional. It is expected that the large exact exchange ratio in RGE2h would help to obtain improved barrier heights for chemical reactions. (This will be studied elsewhere.) To obtain good atomization energies, the PBEsol hybrid functional requires more than 50% exact exchange. However, PBEsol was constructed for solids, and we do not detail the optimization of the PBEsol hybrid in this paper.

The test set of 18 solids¹⁵ was distributed over simple metals, semiconductors, ionic solids, and transition metals, and for this test set PBEsol showed essentially 0% error in the lattice constant, when compared to experimental values extrapolated to absolute zero temperature and corrected for zero-point anharmonic expansion.¹⁵ The experimental low temperature (5 K) lattice constants values are from refs 25 (Li), 26 (Na, K), 27 (Al, Pb, Cu, Rh, Pd, and Ag), and 28 (NaCl). The rest are based on room temperature values from refs 29 (C, Si, SiC, Ge, GaAs, NaF, LiF) and from 26 (LiCl), corrected to the $T = 0$ limit using thermal expansion

Table 1. Errors (kcal/mol) of the Atomization Energies of the AE6 Test Set Calculated with PBE, PBEsol, RGE2, and TPSSh Functionals Using the 6-311G(3df,2p) Basis Set^b

	PBE	PBEsol	PBEsolh	RGE2 ^a	RGE2	RGE2h	RGE2h	RGE2h	RGE2h	TPSSh	expt
μ	0.21951	0.12346	0.12346	0.12346	0.12346	0.12346	0.12346	0.12346	0.12346	—	
β	0.0667	0.0460	0.0460	0.0667	0.0530	0.0530	0.0530	0.0530	0.0530	—	
<i>a</i>	0.00	0.00	0.25	0.00	0.00	0.25	0.30	0.37	0.40	0.10	
SiH ₄	-9.2	1.3	1.5	-8.8	-4.8	-3.1	-2.7	-2.1	-1.8	10.7	322.4
SiO	3.6	12.9	-3.0	2.9	4.3	-8.7	-11.2	-14.4	-16.1	-11.0	192.1
S ₂	13.1	21.9	10.5	16.5	16.2	7.2	5.5	3.2	2.1	3.4	101.7
C ₃ H ₄	16.4	45.1	26.0	18.9	22.4	8.8	6.2	2.7	1.0	0.0	704.8
C ₂ H ₂ O ₂	31.8	64.7	28.0	35.9	38.5	10.2	4.7	-2.4	-6.0	-7.0	633.4
C ₄ H ₈	18.7	69.5	47.7	27.7	33.4	20.5	18.1	14.9	13.3	5.3	1149.0
ME	12.4	35.9	18.4	15.5	18.3	5.8	3.4	0.3	-1.2	0.2	
MAE	15.5	35.9	19.5	18.5	20.0	9.8	8.1	6.6	6.7	6.2	
rms	17.8	44.1	25.4	21.5	23.8	11.1	9.6	8.7	8.9	7.3	
StDev	14.0	28.2	19.1	16.3	16.7	10.4	9.8	9.6	9.7	8.0	
Min	-9.2	1.3	-3.0	-8.8	-4.8	-8.7	-11.2	-14.4	-16.1	-11.0	
Max	31.8	69.5	47.7	35.9	38.5	20.5	18.1	14.9	13.3	10.7	

^a RGE2 exchange + PBE correlation with $\beta = 0.066725$. This choice of β results in slightly too large surface energies, and has negligible influence on the lattice constants compared to the choice of $\beta = 0.0530$. ^b The values of the exchange (μ) and correlation (β) gradient expansion coefficients are shown. The weight of the exact exchange (*a*) is also shown for the hybrid functionals (cf. eq 8).

corrections from ref 27 (Note that a linear extrapolation of the lattice constant from 300 K to 0 K is neither accurate nor used here.) Note that in ref 15 the ZPAE corrections for C, Si, SiC, Ge, GaAs, NaCl, NaF, LiCl, LiF, and MgO are incorrectly given; those values should be multiplied by 2, as corrected in the erratum of ref 12. This small test set is not representative, but a recent study shows³² that the extension of the test set does not radically change the overall statistics.

Our original calculations for solids were made with the periodic-boundary-condition version of the Gaussian³⁰ code. The RGE2 functional is implemented self-consistently into the developmental version of Gaussian, and the lattice constants are computed with optimized geometry. We use the same Gaussian-type orbital (GTO) basis sets as in our earlier work.¹² In order to make the calculations efficient, the small-exponent functions have to be removed from the molecular GTOs and the exponents of the remaining valence functions reoptimized. For details see refs 15 and 31. It was observed that the GTO basis set used in this study makes the lattice constants slightly larger (by 0.01 Å on average) compared to solid state codes like BAND or VASP.³²

The valence electron densities of the 18 solids we have studied have reduced density gradients in the range $0 < s < 2.2$.³² To make the GGA recover the second-order gradient expansion for exchange over a wide range of solid-state-like densities, we have to enhance the gradient expansion beyond the one used in the PBEsol functional. This enhancement is achieved by adding the higher-order term to the denominator of the enhancement factor.

In Table 2 we compare the new RGE2 results with the PBE-GGA, PBEsol, and TPSS lattice constants. The PBEsol is very accurate and produces a mean error (ME) of 0.02 Å for these 18 solids, as noted earlier.^{12,32} The TPSS lattice constants are somewhat too long and cannot compete in accuracy with the PBEsol values. Notice that the TPSS and RGE2 lattice constants are quite similar for simple metals and semiconductors. The RGE2 shows a good performance for transition metals in this test set (actually better than PBEsol). The lesson we take from our PBEsol work is that

Table 2. Strukturbericht Symbols (Str.), Equilibrium Lattice Constants (Å), and Statistical Data of 18 Test Solids Calculated with the GAUSSIAN Program^e

	Strukt.	LSDA	PBEsol	RGE2	PBE	TPSS	Expt.
μ		0.000	0.1235	0.123	0.21951		
β		0.000	0.0460	0.053	0.06673		
Li	A2	3.383	3.453	3.501	3.453	3.475	3.449
Na	A2	4.049	4.159	4.239	4.199	4.233	4.210
K	A2	5.093	5.232	5.354	5.296	5.362	5.212
Al	A1	4.008	4.038	4.052	4.060	4.035	4.020
ME ^a		-0.089	-0.002	0.064	0.029	0.054	
MAE ^b		0.089	0.023	0.064	0.035	0.054	
Cu	A1	3.530	3.578	3.597	3.635	3.593	3.596
Rh	A1	3.791	3.819	3.830	3.871	3.846	3.793
Pd	A1	3.851	3.888	3.897	3.950	3.917	3.877
Ag	A1	3.997	4.045	4.061	4.129	4.076	4.064
ME ^a		-0.040	0.000	0.014	0.064	0.025	
MAE ^b		0.040	0.019	0.015	0.064	0.027	
C	A4	3.537	3.562	3.573	3.579	3.579	3.543
Si	A4	5.410	5.442	5.460	5.479	5.466	5.416
SiC	B3	4.355	4.381	4.395	4.404	4.394	4.342
Ge	A4	5.634	5.693	5.727	5.776	5.744	5.640
GaAs	B3	5.626	5.687	5.723	5.772	5.745	5.638
ME ^a		-0.003	0.037	0.060	0.086	0.070	
MAE ^b		0.009	0.037	0.060	0.086	0.070	
NaCl	B1	5.471	5.611	5.731	5.696	5.696	5.565
NaF	B1	4.505	4.633	4.733	4.700	4.706	4.579
LiCl	B1	4.968	5.072	5.152	5.146	5.113	5.074
LiF	B1	3.904	4.002	4.082	4.063	4.026	3.964
MgO	B1	4.178	4.229	4.266	4.270	4.247	4.184
ME ^a		-0.068	0.036	0.119	0.102	0.084	
MAE ^b		0.068	0.037	0.119	0.102	0.084	
TME ^c		-0.049	0.020	0.067	0.073	0.060	
TMAE ^d		0.050	0.030	0.067	0.074	0.061	

^a Mean error. ^b Mean absolute error. ^c Total mean error. ^d Total mean absolute error. ^e μ and β are the parameters of the exchange and correlation enhancement factors in eqs 2 and 4. The Strukturbericht symbols are used for the structure as follows: A1, fcc; A2, bcc; A4, diamond; B1, rock salt; B3, zinc blend. The experimental (5–50 K) lattice constants values are from refs 25 (Li), 26 (Na, K), 27 (Al, Cu, Rh, Pd, Ag), and 28 (NaCl). The rest are based on room temperature values from refs 29 (C, Si, SiC, Ge, GaAs, NaF, LiF, MgO) and 26 (LiCl), corrected to the $T = 0$ limit using the thermal expansion from ref 27. An estimate of the zero-point anharmonic expansion is subtracted out from the experimental values.³² The best theoretical values are in boldface.

Table 3. Jellium Surface Exchange σ_x and Exchange-Correlation Energies σ_{xc} (erg cm⁻²) for LSDA, PBE, PBEsol ($\kappa = 0.804$, $\mu = 0.1234568$, $\beta = 0.046$), RGE2 ($\kappa = 0.804$, $\mu = 0.1234568$, $\beta = 0.053$), TPSS, Exact, Diffusion Monte Carlo (DMC), and Corrected Random Phase Approximation (RPA+)^f

method	σ	r_s			
		2	3	4	6
LSDA ^a	x	3037	669	222	43.0
PBE ^a	x	2438	468	128	11.8
PBEsol	x	2666	540	162	22.9
RGE2	x	2622	523	153	19.5
TPSS ^a	x	2553	498	141	15.4
exact^b	x	2624	526	157	22
LSDA ^a	xc	3354	764	261	53
PBE ^a	xc	3265	743	252	52
PBEsol	xc	3374	774	267	56
RGE2	xc	3373	771	265	55
TPSS ^a	xc	3380	772	266	55
DMC ^c	xc	3392	768	261	52.5
RPA+ ^d	xc	3413	781	268	54
RGE2xPBEc ^e	xc	3449	797	278	59.5

^a Reference 15. ^b Reference 35. ^c Diffusion Monte Carlo.³⁶ ^d Corrected random phase approximation.³⁷ ^e RGE2 exchange + PBE correlation with $\beta = 0.066725$. This choice of β results in slightly too large surface energies and has negligible influence on the lattice constants but improves atomization energies (cf. Table 1 compared to the choice of $\beta = 0.0530$). ^f r_s is the Wigner-Seitz radius. (1 au = 1.557 10⁶ erg cm⁻²).

good lattice constants can be achieved when the correct Antoniewicz-Kleinman³³ second-order gradient expansion for exchange is recovered *over a wider range of solid-state-like densities than it is in TPSS*. The TPSS meta-GGA already recovers this expansion, but only for solid-like densities that are very slowly varying over space. This observation applies especially for ionic solids, for which TPSS and RGE2 seriously overestimate the lattice constants.¹⁵ A similar observation has been made recently³² for the Armiento-Mattsson 2005 GGA.³⁴

Overall, the performance of our RGE2 functional lies between PBE and TPSS. Transition metals have very slowly varying densities, with a maximum reduced gradient of less than one, while ionic crystals have a maximum reduced gradient around two (2.2).³² To achieve accurate atomization energies, we have to enhance the nonlocality of our functional, but this comes at the price of reduced accuracy for lattice constants of ionic solids at the GGA level.

The surface energies of different approximations were tested on jellium, a model for simple metals in which the electrons are distributed in a positive background truncated at a plane. The density of the bulk region is characterized by the Wigner-Seitz radius, r_s , which stems from the density of the positive background. The exact value of the exchange component of the jellium surface energy is known.³⁵ There is a significant improvement in the exchange energy of a slowly varying density when we pass from PBE to TPSS, and thus the inner part of the surface density profile is better treated as shown in Table 3. The excellent performance of the RGE2 exchange functional is apparent from Table 3. Note that the RGE2 exchange functional has no empirical parameter, and it is better than the similarly nonempirical PBEsol exchange. For the surface exchange-correlation energy, the

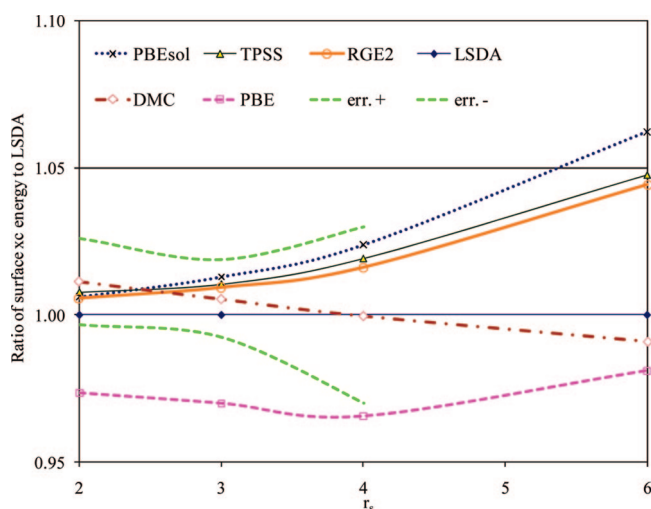


Figure 3. Ratio of calculated surface exchange-correlation energy to that of LSDA, as a function of r_s for various approximations. The upper and lower error bars of the diffusion Monte Carlo (DMC) surface exchange-correlation energy (ref 36), err + and err -, are also shown for $r_s < 4$.

RGE2 results were fitted to the TPSS functional, and they show an excellent agreement with the TPSS functional for whole r_s range in Figure 3. The diffusion Monte Carlo³⁶ and the most precise surface exchange-correlation energy results coming from the random phase approximation (RPA+) with short-range correction³⁷ are also shown in Table 3. Comparison of the results in Tables 2 and 3 shows that the excellent RGE results for jellium surface energies do not guarantee good lattice constants, for a wide range of solids.

IV. Conclusions

We designed a new generalized gradient expansion or GGA, a regularized gradient expansion or RGE2 that recovers the second-order gradient expansion for exchange in the slowly varying limit, in an attempt to obtain good solid-state and molecular properties at the same time from a single GGA. The performance of this functional for molecular atomization energies is better than the performance of PBEsol but worse than that of PBE. For the AE6 atomization test set, we constructed an optimized RGE2 hybrid, with 37% exact exchange and 63% RGE2 exchange. This RGE2h gives reasonable molecular atomization energies with mean absolute error (MAE) of 6.6 kcal/mol (while the quite good nonempirical TPSSh functional has MAE = 6.2 kcal/mol). For lattice constants of solids, the RGE2 functional is worse than the PBEsol functional except for transition metals. Interestingly the overall performance of the RGE2 for solids is similar to TPSS. However this test set of 18 solids is not representative, and thus tests on larger test sets are planned. The correlation gradient expansion coefficient β of the RGE2 correlation was set to obtain TPSS jellium surface exchange-correlation energies in the same way as in PBEsol, but the RGE2 agrees somewhat better with TPSS than PBEsol. Our results show that the excellent RGE2 jellium surface energies do not guarantee good lattice constants, for a wide range of solids.

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