A More Accurate Generalized Gradient Approximation for Solids

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(Dated: September 11, 2018)

We present a new nonempirical density functional generalized gradient approximation (GGA) that gives significant improvements for lattice constants, crystal structures, and metal surface energies over the most popular Perdew-Burke-Ernzerhof (PBE) GGA. The new functional is based on a diffuse radial cutoff for the exchange-hole in real space, and the analytic gradient expansion of the exchange energy for small gradients. There are no adjustable parameters, the constraining conditions of PBE are maintained, and the functional is easily implemented in existing codes.

PACS numbers: 71.15.Mb, 71.45.Gm, 77.80.-e

Kohn-Sham density functional theory (DFT) \cite{1,2} makes it possible to solve many-electron ground-state problems efficiently and accurately. The DFT is exact if the exchange-correlation (XC) energy \(E_{XC}\) were known exactly, but there is no tractable exact expressions of \(E_{XC}\) in terms of electron density. Numerous attempts have been made to approximate \(E_{XC}\), starting with the local (spin) density (LSD) approximation (LDA), which is still widely used. The generalized gradient approximations (GGAs) \cite{3,4,5} are semilocal, seeking to improve upon LSD. Other more complicated approximations are often orbital-dependent or/and nonlocal. They suffer from computational inefficiency; it is much harder to treat them self-consistently and to calculate energy derivative quantities.

The XC energy of LSD and GGAs are

\[
E_{XC}^{LSD}(n↑, n↓) = \int n\{n↑ + n↓\}^{\text{unif}}(r) d^3r,
\]

and

\[
E_{XC}^{\text{GGA}}(n↑, n↓) = \int f(n↑, n↓, \nabla n↑, \nabla n↓) d^3r,
\]

respectively. Here the electron density \(n = n↑ + n↓\), and \(n\{n↑ + n↓\}^{\text{unif}}\) is the XC energy density for the uniform electron gas. LSD is the simplest approximation, constructed from uniform electron gas, and very successful for solids, where the valence electron densities vary relatively more slowly than in molecules and atoms, for which GGAs \cite{3,4,5} achieved a great improvement over LSD. It is well known that LSD underestimates the equilibrium lattice constant \(a_0\) by 1-3\%, and some properties such as ferroelectricity are extremely sensitive to volume. When calculated at the LSD volume, the ferroelectric instability is severely underestimated \cite{4,6,7}. On the other hand, GGAs tend to expand lattice constants. They well predict correct \(a_0\) for simple metals, such as Na and K \cite{8}, however for other materials they often overcorrect LSD by predicting \(a_0\) 1-2\% bigger \cite{9} than experiment. Predicting lattice constants more accurately than LSD remains a tough issue, even for state-of-the-art meta-GGAs; nonempirical TPSS \cite{10} only achieves moderate improvement over PBE, while empirical PKZB \cite{12} is worse than PBE. GGAs are especially poor for ferroelectrics, e.g., PBE \cite{5} predicts the volume and strain of relaxed tetragonal PbTiO\(_3\) more than 10\% and 200\% too large, respectively \cite{13}, and other GGAs \cite{14,15,16} are even worse, as seen in Table I. Another more complicated functional, the nonlocal weighted density approximation (WDA) is also unsatisfactory for this case \cite{13}. To compute these properties correctly, people often constrain volumes at their experimental values \(V_{\text{expt}}\). However, \(V_{\text{expt}}\) is not available for predicting new materials, certain properties are still wrong even at \(V_{\text{expt}}\); theoretically it is more satisfactory to do calculations without any experimental data adjustments.

In order to study finite temperature properties, e.g., ferroelectric phase transitions, effective Hamiltonian and potential models, which are used in molecular dynamics (MD) or Monte Carlo (MC) simulations, have been developed with parameters fitted to first-principles results. When the model parameters are fitted to LSD data, these simulations greatly underestimate the phase transition temperatures \(T_c\) at ambient pressure \cite{16,17,18}, and overestimate if fitted to the GGA results \cite{17}. A simple but more accurate approximation for XC energy is necessary.

Because the magnitude of the exchange energy is much bigger than correlation in most cases, and PBE generally describes the correlation energy with enough accuracy, we focus only on the exchange in this paper. The dimensionless reduced gradient \(s = \nabla n/\sqrt{2/(3\pi^2)r_0^3}n^{1/3}\). The exchange enhancement factor \(F_X\) is defined as

\[
E_X^{\text{GGA}} = \int n\{n\}^{\text{unif}}(r) F_X(s) d^3r,
\]
where the exchange energy density of the uniform electron gas \( \epsilon_{\text{unif}}(n) = -\frac{3}{4\pi^2} (3\pi^2 n)^{1/3} \). The PBE ansatz of \( F_X \) has the general form

\[
F_X = 1 + \kappa - \kappa/(1 + x/\kappa),
\]

where \( \kappa = 0.804 \) to ensure the Lieb-Oxford bound \([15]\), and \( x = \mu s^3 \) with \( \mu = 0.21951 \) to recover the LSD linear response, i.e., as \( s \to 0 \), the exchange gradient correction cancels that for correlation. In the range of interest for real systems \( 0 \leq s \leq 3 \), the PBE \( F_X \) is a simple numerical fit to that of PW91, which is constructed from the gradient expansion of a sharp real space cutoff of the exchange hole \([14, 20]\), plus some exact constraints \([2]\). Unlike atoms and molecules, solids can have a diffuse tail around the exchange-correlation hole, and a diffuse radial cutoff factor \( [1 + (u/u_x)^2] \exp[-(u/u_x)^2] \), where \( u \) is the distance from the hole center and \( u_x \) is the fixed radial cutoff, leads to a smaller \( F_X \) for \( s \gtrsim 1 \) than that of the sharp radial cutoff (inset of Figure 1). This explains why the PBE (PW91) functional improves total energies of atoms and atomization energies of molecules greatly over LSD, but often overcorrects LSD for solids. Two revised versions of PBE, namely revPBE \([14]\) with empirical \( \kappa = 1.245 \) and RPBE \([17]\) with \( F_X = 1 + \kappa - \kappa \exp(-\mu s^2/\kappa) \), further exaggerate \( F_X \) (Figure 1), giving better energies for atoms and molecules, but worse lattice constants of solids (Table I).

The real space cutoff procedure can only give qualitative features of \( F_X \), not the exact behavior because it depends on the detailed approximations of the procedure and fitting to parameters, so other known constraints must be chosen to determine \( F_X \). Usually valence electron densities of solids vary much more slowly than electron densities of atoms and molecules. The choice of \( \mu \) in PBE violates the known gradient expansion of Svendsen and von Barth \([21]\) for slowly varying density systems,

\[
F_X = 1 + \frac{10}{81}p + \frac{146}{2025}q^2 - \frac{73}{405}qp + Dp^2 + O(\nabla^6),
\]

where \( p = s^2 \), \( q = \nabla^2 n/[4(3\pi^2)^{2/3}n^{5/3}] \) is the second order reduced gradient, and \( D = 0 \) is the best numerical estimate. If \( \mu \) is set to \( 10/81 \), \( F_X \) of equation 4 will be lowered. However the behavior of PBE \( F_X \) for small \( s \) needs to be retained because (i) it is necessary to retain cancelation of gradient correction of exchange and correlation as \( s \to 0 \); (ii) \( F_X \) determined by a diffuse radial cutoff is close to that by sharp radial cutoff for small \( s \) (inset of Figure 1). Thus we propose the following ansatz for \( x \) in Equation 4:

\[
x = \frac{10}{81}s^2 + (\mu - \frac{10}{81})s^2 \exp(-s^2) + \ln(1 + cs^4),
\]

where the parameter \( c \) is set to recover the fourth order parameters in Equation 5 for small \( s \). Because a good approximation of \( q \) for slowly varying densities is \( q \approx \frac{2}{3}p \), \( c = \frac{46}{2025} - \frac{73}{405} - \frac{(\mu-10/81)}{81} = 0.0079325 \). Our new functional will be referred to as “WC”, and \( F_X^{\text{WC}} \) still satisfies the four conditions (d)-(g) constraining \( F_X^{\text{PBE}} \). It is nearly identical to \( F_X^{\text{PBE}} \) for \( s \lesssim 0.5 \), and smaller for bigger \( s \), as displayed in Figure 1. Amazingly, the present simple \( F_X^{\text{WC}} \) matches that of the more byzantine TPSS meta-GGA for slowly varying densities very well, which makes use of the kinetic energy density to enforce Equation 5 for small \( p \) and \( q \). Contrasting with earlier attempts such as RevPBE, WC has no adjustable parameters fitted to experimental data, and it is constructed completely from fundamental physical considerations.

We tested the new functional of Equation 5 by computing equilibrium crystal structures and cohesive energies of solids, jellium surface energies, and exchange energies of atoms. We used the plane-wave pseudopotential method (ABINIT4.4.4 \([22]\)) for solids, and an all-electron atomic code for atoms. It is straightforward to implement the current GGA from the PBE pseudopotential code. We used the same configurations for each atom to generate optimized norm-conserving pseudopotentials by the OPIUM code \([23]\) of LSD, PBE, and WC.

First we calculated equilibrium lattice constants \( a_0 \) of 18 solids as tested in Refs. \([10, 11]\). We found LSD underestimates, while PBE overestimates \( a_0 \), and current LSD and PBE errors agree well with previous ones. As seen in Table I WC improves \( a_0 \) significantly over LSD and PBE, even much better than TPSS. Note that lattice constants should be extrapolated to 0 K to compare with DFT results due to thermal expansion. An interesting example is \( a_0 \) of cubic PbTeO\(_3\), which is 3.969 Å at 766 K (ferroelectric phase transition temperature). It reduces
TABLE II: Errors (mean absolute relative error) of calculated equilibrium lattice constants \(a_0\), bulk moduli \(B_0\), and cohesive energies \(E_0\) of 18 tested solids, Li, Na, K, Al, C, Si, SiC, Ge, GaAs, NaCl, NaF, LiCl, LiF, MgO, Cu, Rh, Pd, Ag, at 0 K comparing with experiments \[10\]. TPSS and PKZB data are from Ref. \[10\].

|       | \(a_0^{\text{LSD}}\) | \(a_0^{\text{PBE}}\) | \(a_0^{\text{WC}}\) | \(a_0^{\text{TPSS}}\) | \(a_0^{\text{PKZB}}\) |
|-------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Error (%) | 1.74 | 1.30 | 0.29 | 0.83 | 1.65 |

|       | \(B_0^{\text{LSD}}\) | \(B_0^{\text{PBE}}\) | \(B_0^{\text{WC}}\) | \(B_0^{\text{TPSS}}\) | \(B_0^{\text{PKZB}}\) |
|-------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Error (%) | 12.9 | 9.9 | 3.6 | 7.6 | 8.0 |

|       | \(E_0^{\text{LSD}}\) | \(E_0^{\text{PBE}}\) | \(E_0^{\text{WC}}\) |
|-------|----------------------|----------------------|----------------------|
| Error (%) | 15.2 | 5.1 | 5.2 |

TABLE III: Equilibrium structural parameters for two ferroelectrics: tetragonal \(P4mm\) \(\text{PbTiO}_3\) (PT) and rhombohedral \(R3m\) \(\text{BaTiO}_3\) (BT). The atom positions \(u_z\) are given in terms of the lattice constants.

|       | LSD | PBE | WC | Expt. |
|-------|-----|-----|-----|-------|
| PT \(V_0\) (Å\(^3\)) | 60.37 | 70.54 | 63.47 | 63.09\(^a\) |
| \(c/a\) | 1.046 | 1.239 | 1.078 | 1.071\(^a\) |
| \(u_z\) (Pb) | 0.0000 | 0.0000 | 0.0000 | 0.0000\(^b\) |
| \(u_z\) (Ti) | 0.5235 | 0.5532 | 0.5324 | 0.538\(^b\) |
| \(u_z\) (O\(_1\)) | 0.5886 | 0.6615 | 0.6106 | 0.612\(^b\) |
| \(u_z\) (O\(_2\)) | 0.0823 | 0.1884 | 0.1083 | 0.112\(^b\) |
| BT \(V_0\) (Å\(^3\)) | 61.59 | 67.47 | 64.04 | 64.04\(^a\) |
| \(\alpha\) | 89.91\(^c\) | 89.65\(^c\) | 89.86\(^c\) | 89.87\(^c\) |
| \(u_z\) (Ba) | 0.0000 | 0.0000 | 0.0000 | 0.0000\(^b\) |
| \(u_z\) (Ti) | 0.5235 | 0.5532 | 0.5324 | 0.538\(^b\) |
| \(u_z\) (O\(_1\)) | 0.5886 | 0.6615 | 0.6106 | 0.612\(^b\) |
| \(u_z\) (O\(_2\)) | 0.0823 | 0.1884 | 0.1083 | 0.112\(^b\) |

\(\alpha\) = 3.971 Å at 0 K by extrapolation \[24\]. \(a_0^{\text{PBE}} = 3.971\) Å is 1% larger, whereas \(a_0^{\text{WC}} = 3.933\) Å, in excellent agreement with the extrapolated data. Also note that the zero-point quantum fluctuations are not included in DFT calculations, which would expand \(a_0\) about 0.2%. WC also predicts more accurate bulk moduli for these materials than LSD and PBE (Table I). For cohesive energies, WC is nearly as accurate as PBE, and much better than LSD (Table III). These results prove that our simple model of GGA is very suitable for solids.

For the ground-state structures of polarized ferroelectrics, the lattice strain must be optimized together with atomic positions. Unlike cubic systems, a large volume for a polarized ferroelectric material favors large strain and atomic displacements, and large strain and atomic displacements lead to even larger volumes. This causes PBE to overestimate the volume of tetragonal \(\text{PbTiO}_3\) by more than 10%, whereas the error is only 3% for the cubic structure. Table III summarizes the LSD, PBE, and WC results of fully relaxed tetragonal \(\text{PbTiO}_3\) and rhombohedral \(\text{BaTiO}_3\). It shows that WC predicts highly accurate volumes, strains, and atomic displacements, whereas LSD and PBE underestimate and overestimate these values, respectively. If their model parameters are fitted to first-principles results using WC, MD or MC simulations are expected to determine ferroelectric phase transition temperatures and other properties more accurately.

It is well known that LSD fails to predict the correct ground states for certain materials, e.g., magnetic bcc iron \[28\] and \(\alpha\)-quartz \[29\], and PBE can eliminate this error. WC predicts correct ground states for both iron and quartz with smaller energy differences than PBE, resulting in lower transition pressures. For iron, the transition (bcc to hcp) pressure of 10 GPa is rather close to experiment, but for quartz (\(\alpha\) to stishovite), the WC result of 2.6 GPa is not sufficient to correct LSD. Since the stishovite phase is much more compact and stiffer than the \(\alpha\) phase, the phonon contributions to energy could increase the energy difference greatly. However by performing first-principles linear response lattice dynamics calculations we find that the vibration zero point energy difference is only 0.015 eV/\(\text{SiO}_2\), because the \(\alpha\) phase has high frequency modes the stishovite phase lacks, in addition to low frequency modes. These results indicate that a better correlation functional for WC is also needed.

Another interesting case is the weakly interacting molecular bonding systems. We calculated the hydrogen bond strength in ice for a periodic Bernal-Fowler Ih model \[30, 31\]. The WC sublimation energy of 0.73 eV per \(\text{H}_2\text{O}\) (the measured data is 0.61 eV \[32\], excluding the zero-point vibration) is much better than LSD of 1.07 eV, but not as good as PBE of 0.63 eV, as shown in Fig-

FIG. 2: Sublimation energies of Bernal-Fowler periodic model of ice Ih.

\(^a\)Low temperature data, Ref. \[22\].
\(^b\)Room temperature data, Ref. \[24\].
\(^c\)Low temperature data, Ref. \[25\].
RPBE is excellent for atoms, but poorer for solids than less accurate for atoms than PBE; on the other hand, functional, WC performs excellently for solids, but it is ideal for accuracy for the same system. Using PBE correlation constructed from different situations perform with different accuracy against the available most accurate as PBE. Therefore, a proper treatment of correlation would make WC XC energies of atoms as accurately as LSD against the exact value [32].

Furthermore, a better correlation functional will improve the XC energy and potential also, and one can construct a correlation more compatible with our functional of exchange than PBE. In this way, the accuracy of a simple second rung of the ladder of XC approximations, GGA, could approach that of the more complicated third rung approximation, meta-GGA.

We have constructed a new GGA which is more accurate for solids than any existing GGA and meta-GGA. It has a very simple form without any empirical parameters, and it is ideal for ab initio calculations of certain materials, e.g., ferroelectrics, for which exceptionally high accuracy is needed. It can be generalized to make a GGA more accurate for atoms, molecules, and solids than PBE.

We are indebted to L. Almeida and J. P. Perdew for sending us the jellium code. We thank E. J. Walter, H. Krakauer, P. Schultz, and A. E. Mattsson for helpful discussions. This work was supported by the Center for Piezoelectrics by Design (CPD) and the Office of Naval Research (ONR) under ONR Grants No. N00014-02-0-0506.

As argued by Perdew 2, in an extended system such as metal surface the exact hole may display a diffuse long-tail behavior: an emitted electron’s exchange-correlation tail behavior: an emitted electron’s exchange-correlation energy

\[ \sigma \]

against the exact value [32]. We have shown that exchange enhancement factors \( F_X \) constructed from different situations perform with different accuracy for atoms than PBE; on the other hand, RPBE is excellent for atoms, but poorer for solids than PBE. It seems impossible to make a GGA which is more accurate than PBE for both solids and atoms simultaneously because \( F_X \) is a function only of the reduced gradient \( s \). Our calculations show that \( F_X \) also depends on the variation of \( |\nabla n| \). Since high density systems often have large variations and low density systems often vary slowly, we propose that a GGA having \( F_X = F_X(s, r_s) \), just like the gradient correlation correction, could be universally more accurate for atoms, molecules, and solids than PBE. The additional parameters of \( F_X(s, r_s) \) can be fitted to quantum Monte Carlo simulations for specific materials, or determined by constraints at \( r_s \to 0 \) and \( r_s \to \infty \) from other theoretical considerations.

We have constructed a new GGA which is more accurate for solids than any existing GGA and meta-GGA. It has a very simple form without any empirical parameters, and it is ideal for ab initio calculations of certain materials, e.g., ferroelectrics, for which exceptionally high accuracy is needed. It can be generalized to make a GGA more accurate for atoms, molecules, and solids than PBE.

Finally, we compared calculated exchange energies of 5 noble-gas atoms with the Hartree-Fock (HF) results 5. The mean errors for LSD, PBE, RPBE, and WC are 8.77%, 0.89%, 0.18%, and 2.01%, respectively. Comparing the magnitude of \( F_X \) of these GGA as illustrated in Figure 1, one can conclude that among these choices a GGA with bigger \( F_X \) predicts better \( E_X \) of atoms. Although WC is constructed for slowly varying densities, it improves exchange energies of atoms over LSD significantly. Furthermore, a proper treatment of correlation functional would make WC XC energies of atoms as accurate as PBE.

We have shown that exchange enhancement factors \( F_X \) constructed from different situations perform with different accuracy for the same system. Using PBE correlation functional, WC performs excellently for solids, but it is less accurate for atoms than PBE; on the other hand, RPBE is excellent for atoms, but poorer for solids than PBE. It seems impossible to make a GGA which is more accurate than PBE for both solids and atoms simultaneously because \( F_X \) is a function only of the reduced gradient \( s \). Our calculations show that \( F_X \) also depends on the variation of \( |\nabla n| \). Since high density systems often have large variations and low density systems often vary slowly, we propose that a GGA having \( F_X = F_X(s, r_s) \), just like the gradient correlation correction, could be universally more accurate for atoms, molecules, and solids than PBE. The additional parameters of \( F_X(s, r_s) \) can be fitted to quantum Monte Carlo simulations for specific materials, or determined by constraints at \( r_s \to 0 \) and \( r_s \to \infty \) from other theoretical considerations. In addition, a better correlation functional will improve the XC energy and potential also, and one can construct a correlation more compatible with our functional of exchange than PBE. In this way, the accuracy of a simple second rung of the ladder of XC approximations, GGA, could approach that of the more complicated third rung approximation, meta-GGA.

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| \( r_s \) (bohr) | LSD | PBE | TPSS | WC | exact |
|----------------|-----|-----|------|----|-------|
| 2.00           | 3037| 2438| 2553 | 2519| 2624  |
| 2.30           | 1800| 1395| 1469 | 1452| 1521  |
| 2.66           | 1051| 770 | 817  | 809 | 854   |
| 3.00           | 669 | 468 | 497  | 497 | 526   |
| 3.28           | 477 | 318 | 341  | 341 | 364   |
| 4.00           | 222 | 128 | 141  | 141 | 157   |
| 5.00           | 92  | 40  | 47   | 47  | 57    |
| 6.00           | 43  | 12  | 15   | 15  | 22    |

Error (%) 36.7 16.7 9.4 9.8

TABLE IV: Jellium surface exchange energies (\( \sigma_X \), in erg/cm\(^2\)) computed using the LSD orbitals and densities. LSD and PBE values are from Ref. [12], and TPSS values are from Ref. [10]. The last row is the mean absolute relative errors against the exact value [32].
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