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## The AM05 density functional applied to solids

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We show that the AM05 functional [Armiento and Mattsson, Phys. Rev. B **72**, 085108 (2005)] has the same excellent performance for solids as the hybrid density functionals tested in Paier *et al.* [J. Chem. Phys. **124**, 154709 (2006); **125**, 249901 (2006)]. This confirms the original finding that AM05 performs exceptionally well for solids and surfaces. Hartree–Fock hybrid calculations are typically an order of magnitude slower than local or semilocal density functionals such as AM05, which is of a regular semilocal generalized gradient approximation form. The performance of AM05 is on average found to be superior to selecting the best of local density approximation and PBE for each solid. By comparing data from several different electronic-structure codes, we have determined that the numerical errors in this study are equal to or smaller than the corresponding experimental uncertainties. © 2008 American Institute of Physics. [DOI: [10.1063/1.2835596](https://doi.org/10.1063/1.2835596)]

### I. INTRODUCTION

Density functional theory<sup>1,2</sup> (DFT) has become the foundation of most large-scale quantum mechanical simulations. The success stems from the theory's good quantitative results for a broad range of systems in combination with its relatively low computational cost. At the core of every Kohn–Sham DFT calculation lies the exchange–correlation (XC) functional. It is, in principle, the only limiting factor for the accuracy of the calculations.<sup>6,3</sup> The development of new functionals is, therefore, of utmost importance to the progress of computational materials science, -physics, -chemistry, and -biology. Despite the importance, significant improvements of the exchange and correlation treatment have been few. Since DFT is increasingly being employed for large systems (several hundred atoms) and for long (tens of picoseconds) molecular dynamics (MD) simulations, the trade-off between speed and accuracy is arising as an additional major concern in functional development.

In this article, we assess the performance of the Armiento–Mattsson 2005 functional<sup>3</sup> (AM05) for a large set of crystalline solids. We show that AM05 systematically improves upon earlier functionals of the same class [the density and gradient based functionals local density approximation (LDA),<sup>2</sup> PBE,<sup>4</sup> BLYP,<sup>5,6</sup> and RPBE<sup>7</sup>]. The AM05 functional, in fact, performs as well as the hybrid functionals PBE0

(Refs. 8 and 9) and HSE06,<sup>10</sup> see Table I. In addition to two functionals commonly used for solid-state applications, LDA and PBE, we chose to include BLYP and RPBE because of the large and growing interest in water–solid interactions.<sup>14</sup> PBE and BLYP are both used extensively for water<sup>14–19</sup> and RPBE has been suggested to give a water structure in good agreement with experimental results.<sup>15</sup> The performance of AM05 for water will be presented elsewhere,<sup>20</sup> but preliminary results show that the behavior is similar to that of PBE. For water–solid interactions to be modeled correctly, however, it is crucial to model the bulk solid well to begin with. Crystallization of ice on a substrate is one example. Formation of ice depends sensitively on the matching of lattices, hence, the lattice constant of the solid has to be described with high accuracy.

While the XC functional determines the fundamental *accuracy* of the calculation, there is a second source of errors, the numerical *precision* in solving the Kohn–Sham equations. Implementation-related approximations, such as basis sets, pseudopotentials, approximate matrix diagonalization methods, plane-wave cutoff energies, etc. (see, e.g., Ref. 21) can all be successively improved by increasing the computational expense (i.e., by “converging” the calculations). The concept of precision is particularly important in the area of functional development. When the differences between functionals are small,<sup>22,23</sup> the precision of the calculations has to be high enough to resolve them.

In the following, we will give a brief theoretical background that covers the different functionals used in our study. Following this, we present a number of calculations of lattice constants and bulk moduli. Finally, the results are analyzed and discussed.

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TABLE I. Mean error (ME), mean absolute error (MAE), and root mean square error (RMSE) for lattice constants  $a_0$  (Å) and bulk moduli  $B_0$  (GPa), for the functionals tested in this work [AM05, PBE, LDA, RPBE, BLYP, and the best of LDA or PBE (LoP) with respect to lattice constant or bulk modulus] and in Ref. 10 [PBE0, HSE06, and PBE, here denoted as PBE (\*)]. We have used VASP 5.1 (Refs. 10–13) and used the same PAW core potentials as were employed in Ref. 10. The excellent agreement between the present results and those of and Ref. 10 can be seen by comparing PBE and PBE (\*). Of the nonhybrid functionals, only AM05 performs as well as the hybrids. However, the computational cost using AM05 is only a fraction of that using hybrids.

	$a_0$ (Å)			$B_0$ (GPa)		
	ME	MAE	RMSE	ME	MAE	RMSE
AM05	0.001	0.025	0.033	-4.48	8.10	11.2
PBE0	0.007	0.022	0.029	-0.1	7.9	11.3
HSE06	0.010	0.023	0.030	-1.6	8.6	12.8
LoP ( $a_0$ )	0.006	0.040	0.048	-6.67	11.6	16.6
LoP ( $B_0$ )	-0.003	0.049	0.053	-2.45	7.26	9.79
PBE (*)	0.039	0.045	0.054	-12.3	12.4	16.4
PBE	0.039	0.046	0.056	-14.1	14.2	18.3
LDA	-0.070	0.070	0.082	7.48	10.7	15.2
RPBE	0.090	0.091	0.113	-17.9	20.5	24.7
BLYP	0.093	0.100	0.114	-26.0	26.1	32.2

## II. THEORETICAL BACKGROUND

In the Kohn–Sham DFT computational scheme,<sup>2</sup> the ground state electron energy is obtained via the solution of the Kohn–Sham (KS) equations. These equations resemble the Hartree–Fock (HF) equations. However, whereas the Hartree–Fock equations have a fully nonlocal exchange potential, the KS equations instead have an XC potential  $v_{xc}(\mathbf{r})$  that is diagonal and local in real space. This locality means that the equations are solved with significantly less computational expense. Also, in difference to the Hartree–Fock equations, the transformation of the many-body electron problem into the KS equations introduces no approximations in itself. All correlation effects can *formally* be accounted for within the XC potential  $v_{xc}(\mathbf{r})$ . In practice, the crucial question is how good the approximation of this quantity is.

The XC potential  $v_{xc}(\mathbf{r})$  is obtained through functional differentiation of the DFT XC energy  $E_{xc}[n]$  as a functional of the ground state electron density  $n(\mathbf{r})$ . The XC energy is itself obtained from an integration of the exchange–correlation energy per particle  $\epsilon_{xc}(\mathbf{r};[n])$ ,

$$E_{xc}[n] = \int n(\mathbf{r}) \epsilon_{xc}(\mathbf{r};[n]) d\mathbf{r}. \quad (1)$$

A DFT XC functional is usually understood to mean an approximation to  $\epsilon_{xc}([n];\mathbf{r})$ . This quantity is further split in separate exchange and correlation parts  $\epsilon_{xc} = \epsilon_x + \epsilon_c$ . This separation originates from the choice that the exchange part should give the energy obtained from the Hartree–Fock exchange expression when the one-particle orbitals  $\phi_i(\mathbf{r})$  obtained from solving the KS equations are inserted (in hartree atomic units, for a spin-unpolarized system, i.e., spin up and down orbitals are always filled equally),

$$\epsilon_x(\mathbf{r};[n]) = - \int \frac{1}{n(\mathbf{r})|\mathbf{r}-\mathbf{r}'|} \left| \sum_i^{\text{occ}} \phi_i(\mathbf{r}') \phi_i^*(\mathbf{r}) \right|^2 d\mathbf{r}'. \quad (2)$$

However, any transformation, e.g., by integration by parts, of Eq. (1), gives alternative definitions of the exchange energy per particle<sup>24</sup> that are equally valid.

### A. The local density approximation

The LDA XC functional was presented already in the early works on DFT.<sup>2</sup> LDA obtains the exchange energy from that of a uniform electron gas having a density equal to the local density  $n(\mathbf{r})$  at each spatial point  $\mathbf{r}$ . Using this *model system*, the exchange energy can be derived exactly, giving the following exchange energy per particle,

$$\epsilon_x^{\text{LDA}}(n(\mathbf{r})) = - \frac{3}{4\pi} (3\pi^2 n(\mathbf{r}))^{1/3}. \quad (3)$$

The correlation energy per particle  $\epsilon_c^{\text{LDA}}$  is obtained as a parametrization of quantum Monte Carlo data<sup>25</sup> for the uniform electron gas at different densities. In this work we use the parameterization of Perdew and Wang<sup>26</sup> for the all-electron full-potential calculations performed with the computer code named RSPT and that of Perdew and Zunger<sup>27</sup> for the VASP calculations, but these and other parameterizations are largely equivalent.

Despite its simple construction, LDA has proven successful for many applications, in particular, for solids. To improve upon the LDA form, more degrees of freedom than only the local value of the electron density  $n(\mathbf{r})$  must be introduced in the approximation for the XC energy per particle. The usual way to extend the LDA form is to introduce the electron density gradient  $\nabla n(\mathbf{r})$ , giving a generalized gradient approximation (GGA) form for the XC energy approximation,

$$E_{xc}[n] = \int n(\mathbf{r}) \epsilon_{xc}^{GGA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) d\mathbf{r}. \quad (4)$$

Historically, attempts were made to use a straightforward expansion of the XC energy in the density to produce a systematic improvement of LDA of this form. However, the outcome was disappointing and generally did not improve upon LDA results. Instead, several other approaches have been pursued. The ones important for this work are briefly discussed in the following sections.

## B. Functionals from model systems, the AM05 functional

The method of employing model systems builds upon the strength of LDA: The exchange and correlation energy expressions stem from a single *model system*, the uniform electron gas, for which the exact results are known. This leads to an internal consistency between the exchange and correlation approximations, which makes the combined XC quantity more widely applicable than the individual approximations. We refer to this property as “compatible” exchange and correlation functionals. The compatibility manifests itself as a strong cancellation of errors between the exchange and correlation parts of LDA.

Kohn and Mattsson discussed the creation of a XC functional from a surface-oriented model system and its possible combination with another treatment where this model was unsuitable.<sup>28,29</sup> The approach was formalized and generalized in the subsystem functional scheme by Armiento and Mattsson.<sup>24</sup> The idea is to create separate functionals from different model systems and merge them using a density functional index<sup>30</sup> that locally determines the nature of the system. These ideas were made concrete in the AM05 functional.<sup>3</sup> It involves the following two model systems: For regions that are locally bulklike, the uniform electron gas is used; for regions that are locally surfacelike, a surface functional is derived from the Airy gas<sup>28</sup> in combination with the jellium surfaces.<sup>31</sup>

The AM05 surface exchange functional is a parameterization of the Airy electron gas data.<sup>28</sup> Such a parameterization was made by Vitos *et al.*,<sup>32</sup> but the AM05 exchange functional improves on it by imposing the correct limiting behavior for large scaled density gradients. The local Airy approximation (LAA) parameterization used in AM05 is given by

$$\epsilon_x^{LAA}(n(\mathbf{r}), |\nabla n(\mathbf{r})|) = \epsilon_x^{LDA}(n(\mathbf{r})) F_x^{LAA}(s), \quad (5)$$

where the scaled density gradient  $s = |\nabla n(\mathbf{r})| / [2(3\pi^2)^{1/3} n^{4/3}(\mathbf{r})]$ , and the refinement function  $F_x^{LAA}(s)$  is defined as

$$F_x^{LAA}(s) = (cs^2 + 1)/(cs^2/F_x^b + 1), \quad (6)$$

where  $c=0.7168$  is a fitted constant. The form of  $F_x^{LAA}(s)$  is chosen to impose a correct uniform limit onto  $F_x^b$ , which is constructed as an analytical interpolation between two known limits of the Airy refinement function as discussed below.

An effective scaled  $z$  coordinate in the Airy gas model,<sup>3,28</sup> exact in the limit of high values of  $s$ , can be defined as

$$\tilde{\zeta}(s) = \left[ \frac{3}{2} W \left( \frac{s^{3/2}}{2\sqrt{6}} \right) \right]^{2/3}, \quad (7)$$

where  $W$  is the Lambert  $W$  function.<sup>33</sup> (This function can be calculated to machine accuracy by a few iteration steps implemented in a short piece of code; a routine is available from the authors.)

The properties of  $\tilde{\zeta}(s)$  makes it possible to create an Airy refinement function that simultaneously satisfy both the true high and low  $s$  limits,

$$F_x^b = -1/[\epsilon_x^{LDA}(\tilde{n}_0(s)) 2\tilde{\zeta}(s)], \quad (8)$$

where  $\tilde{\zeta}(s)$  is a suitable interpolation between the two limits,

$$\tilde{\zeta}(s) = ([ (4/3)^{1/3} 2\pi/3 ]^4 \tilde{\zeta}(s)^2 + \tilde{\zeta}(s)^4)^{1/4}, \quad (9)$$

and where  $n_0(s)$  is an effective density defined from the effective  $z$  coordinate  $\tilde{\zeta}(s)$ ,

$$\tilde{n}_0(s) = \frac{\tilde{\zeta}(s)^{3/2}}{3\pi^2 s^3}. \quad (10)$$

For a fully compatible setup, the  $\epsilon_x^{LAA}$  exchange functional should be combined with a correlation functional obtained as a parameterization of, e.g., quantum Monte Carlo data for the Airy gas system. However, with no such data available, Armiento and Mattsson derived a semicompatible surface correlation from the XC data available for jellium surface models, based on the idea that both the Airy gas and jellium surface models are related to similar surface physics. The basic idea is to correct for the difference in surface correlation, as compared to bulk correlation, by a simple scaling factor to the LDA expression. The scaling factor was obtained from a fit to the combined exchange and correlation energies for surface jellium data,<sup>34</sup> giving

$$\epsilon_c(\mathbf{r}; [n]) = \gamma \epsilon_c^{LDA}(n(\mathbf{r})), \quad \gamma = 0.8098. \quad (11)$$

This fit used the Perdew–Wang parametrization of the LDA correlation,<sup>26</sup> which should thus always be used within AM05.

The surface functional is combined via the subsystem functional scheme with LDA for bulklike regions using a density index,

$$X = 1 - \alpha s^2 / (1 + \alpha s^2), \quad (12)$$

where  $\alpha=2.804$  was obtained simultaneously with  $\gamma$  in the fit to surface jellium energy data [cf. comment to Eq. (11)]. The final composed expression for the AM05 exchange and correlation functionals are

$$\begin{aligned} \epsilon_x^{LAA}(\mathbf{r}; [n]) &= \epsilon_x^{LDA}(n(\mathbf{r})) [X + (1-X) F_x^{LAA}(s)], \\ \epsilon_c^{LAA}(\mathbf{r}; [n]) &= \epsilon_c^{LDA}(n(\mathbf{r})) [X + (1-X) \gamma]. \end{aligned} \quad (13)$$



Note that, although AM05 is of the same form as a GGA, and can be easily implemented<sup>35</sup> in a code using the same input quantities as, e.g., PBE does, it stems from a different theoretical background than functionals originally referred to as GGAs (PW91, BLYP, and PBE).

The AM05 functional is the first functional constructed according to the subsystem functional scheme. It can be seen as a consistent improvement over LDA in the sense that it reproduces the exact XC energy for *two* types of model systems: The uniform electron gas and the jellium surfaces, describing two situations with fundamentally different physics. The subsystem functional approach outlines a series of further improved functionals, achieved by keeping the current exact XC model systems and adding others. In the application of AM05 to the solid-state systems of the current work (see Table I), we see how this formal improvement over LDA also translates into significantly improved numerical results.

### C. Constraint-based construction, the PBE functional

When LDA was analyzed to better understand its success for systems dominated by electron densities far from uniform, it was observed that LDA fulfills a number of exact constraints that one can show also the exact XC functional fulfills. Several works, most prominently the ones of Perdew and co-workers, focus on this observation to argue that improved functionals can be constructed by retaining the constraints LDA fulfills and adding new ones.

One of the most prominent examples of a GGA XC functional is the popular and successful one of Perdew, Burke, and Ernzerhof (PBE).<sup>4</sup> For systems such as atoms and molecules, PBE constitutes a significant improvement over LDA. The derivation explicitly focuses on seven constraints that are fulfilled by the construction. Some of these are argued to be the energetically significant constraints of LDA, and others are new ones fulfilled in addition (see, e.g., the discussion in Ref. 36). However, despite PBE being constructed to fulfill the important constraints of LDA, it is not a uniform improvement on LDA for solids. Rather, for combined XC, PBE is, for example, less accurate than LDA for surface jellium,<sup>36</sup> a traditional solid-state model system. Although PBE often gives lattice constants in better agreement with experiments than LDA does, the same is not true for the bulk moduli (see Table I).

Since the publication of AM05 in 2005, other authors have also attempted to create functionals with improved performance for solids. Wu and Cohen's approach<sup>37</sup> results in the exchange term having a weaker dependence on the scaled gradient  $s$  than the PBE exchange has; a relatively weak  $s$  dependence is a property of both LAG<sup>32</sup> and AM05.<sup>3,32</sup> A very recent functional by Perdew *et al.*<sup>38</sup> also has an exchange term with a weak  $s$  dependence. For correlation, they follow closely the construction of AM05, and fit to the combined exchange and correlation energy for surface jellium. The resulting functional gives values close to AM05 over a range of  $s$  typically encountered in real solids, and, thus, we predict that this new functional will show a performance similar to that of AM05.

By allowing additional degrees of freedom in the XC energy per particle approximation than the gradient of the density, as used in the GGA form Eq. (4), further constraints can be satisfied. This leads to the concept of meta-GGAs which include, e.g., the kinetic energy density of the KS orbitals. The TPSS<sup>39</sup> meta-GGA functional is reported to give improved results over PBE, but since the testing was done on a slightly different set of solids and with a different code, it is not possible to make direct comparisons in this work (see Sec. IV B).

### D. Empirical construction, the BLYP and RPBE functionals

An alternative to the constraint-based functional construction is the more pragmatic approach of empirical functionals. The governing principle is that good exchange and correlation functionals can be obtained from suitable generic expressions fitted to known energies. Traditionally, this approach has been more prevalent for functionals aimed at chemical systems than solid-state systems; perhaps due to the more readily available high-quality total energy data of, e.g., atoms that can be used for such fitting.

One of the most widely used functionals created from this idea is the BLYP XC functional. It is composed by the B88 exchange functional<sup>5</sup> and the LYP correlation.<sup>6</sup> Both these functionals rely on fits of their free parameters to atomic data. The BLYP functional has proven very successful for various applications in chemistry. However, from a theoretical standpoint, the LYP functional has been strongly criticized for a number of shortcomings: (i) It does not reproduce LDA in the limit of slowly varying densities; (ii) it gives zero correlation energy for any fully spin-polarized system; and (iii) its derivation involves theoretical problems related to non-normalized wavefunctions.<sup>40</sup> BLYP was implemented in VASP as a part of a recent study of the properties of B3LYP.<sup>41</sup>

There have also been attempts to turn PBE into a semi-empirical functional. Zhang and Yang created revPBE by giving up one of the PBE constraints, and instead refit one of its parameters to data on atoms ranging from helium to argon.<sup>42</sup> Hammer *et al.* observed that the refit not only gave improved chemisorption energies,<sup>7</sup> but also that this improvement could still be achieved without giving up any of the original PBE constraints by changing the form of the expression for the exchange functional. The result, the RPBE functional,<sup>7</sup> is not explicitly empirical in the sense that it does not directly involve any fits. However, the new exchange functional form was chosen because it reproduces relevant behavior of the exchange of revPBE, which was fitted to atomic data. As opposed to the LAG and AM05 functionals, the dependence on the scaled gradient  $s$  is stronger for the RPBE functional than for the PBE functional. Because of this, RPBE is not expected to improve on PBE for solid-state systems. On the contrary, because of the relatively strong  $s$  dependence the volume should increase compared to the PBE functional. This is indeed what we find in our tests (see Table I). It is, however, still relevant to include RPBE in the comparisons, since the choice of functional for mixed systems involves a trade-off with the goal of perform-

ing well enough for all parts. For such applications, our results may help assess how large the trade-off is in using RPBE for the solids.

### E. Hybrid functionals

Hybrid functionals, which are characterized by the admixture of a certain amount of nonlocal Fock exchange to a part of local or semilocal DFT exchange, are extensively applied in the field of quantum chemistry. Results obtained using hybrid functionals are usually in significantly better agreement with experiments than those obtained using local or semilocal DFT exchange-correlation functionals (see, e.g., Ref. 43).

Becke was the first to successfully formulate a true Hartree-Fock/DFT hybrid scheme, known as “half-and-half functional.”<sup>44</sup> In a subsequent publication, the semiempirical three-parameter hybrid functionals were introduced.<sup>45</sup> Although Becke’s concept is motivated by the adiabatic connection formula for the exchange-correlation energy,<sup>46–49</sup> the free parameters are determined by a least-squares fit to experimental atomization energies, electron and proton affinities, and ionization potentials of atomic and molecular species in the G2 test set. The B3LYP hybrid functional has become one of the most popular semiempirical hybrid functionals in computational chemistry.

In Ref. 41, the performance of the B3LYP hybrid functional applied to crystalline solids is scrutinized. There, Paier *et al.* show that B3LYP performs significantly worse than even simpler and computationally less expensive gradient corrected functionals (such as PBE) for the prediction of almost any relevant property (lattice constants, bulk moduli, or cohesive energies) of systems containing elements beyond the second row. Moreover, cohesive energies for metals are wrong by up to typically 50%.<sup>41</sup> The bad performance for metals is not surprising since the B3LYP functional does not describe the homogeneous electron gas exactly.

A concept to rationalize the amount of Fock exchange admixed to the standard DFT exchange energy was devised by Perdew and co-workers.<sup>8,50,51</sup> Hybrid functionals motivated by this work are, often termed nonempirical or parameter-free and can be based on GGAs (PBE0, Refs. 9 and 52) or meta-GGAs (TPSSH, Ref. 53). The accuracy of nonempirical hybrid functionals has been shown to be not far from that of semiempirical ones for molecular systems. The way the functionals are derived and the lack of empirical parameters fitted to specific properties make these functionals applicable to both quantum chemistry and condensed matter physics. Comprehensive studies of the performance of PBE0<sup>8,9</sup> and HSE06<sup>55</sup> for crystalline solids were published recently.<sup>10,41,54,55</sup>

A major limitation of hybrid schemes, however, is a steep increase in computational cost for periodic systems. Exact exchange HF calculations are typically an order of magnitude slower than local or semilocal density functional calculations. The actual difference in computational cost depends on program package and the electronic structure of the system (metallic, semiconducting, or insulating). At present,

the applicability of hybrids to large systems and/or long MD simulations is substantially limited by computational resources.

## III. RESULTS

### A. VASP calculations

Our VASP results are summarized in Tables II and III. The pseudopotential, plane-wave calculations were done with VASP 5.1,<sup>10,11,13</sup> using projector augmented wave (PAW) core potentials.<sup>56</sup> We applied the same PAW cores as those used by Paier *et al.* in their assessment of hybrid functionals for solids.<sup>10</sup> The PAW implementation in VASP 5.1 allows use of multiple XC functionals on the same set of core potentials<sup>13</sup> while retaining high precision. Although the core wave functions are frozen in the configuration determined as the PAW core is constructed (say, an LDA atom), the core-valence interaction is consistently recalculated with the selected functional. Transferability errors are hence reduced.<sup>13</sup> By performing the AM05 and BLYP calculations on both the LDA and PBE cores, we conclude that the errors thereby introduced are insignificant. In addition, we did full-potential all-electron calculations for all solids, the results of which confirm that the PAW cores developed for VASP are of very high fidelity.

The  $k$ -point integration was performed using the tetrahedron method with Blöchl corrections<sup>57</sup> on an  $18 \times 18 \times 18$  uniform grid<sup>58</sup> centered at the gamma point. All real-space cells are cubic with two atoms for bcc, four atoms for fcc, and eight atoms for the zinc blende and diamond cells. We applied energy cutoffs ranging between 600 and 1000 eV: 600 eV (Al, Ag, Pd, Rh, Cu, GaAs, GaP), 800 eV (Na, NaF, NaCl, MgO, SiC, Si, C, GaN, BN, BP), and 1000 eV (Li, LiF, LiCl) with a convergence criterion of  $1.0 \times 10^{-5}$  eV for the self-consistent loop. The precision in the calculations is thus overall very high. The PBE results can be directly compared to those of Paier *et al.*;<sup>10</sup> the discrepancies are minute and caused by slight differences in the volume range governing the Murnaghan fits. None of the differences affect any conclusions.

### B. RSPT calculations

To confirm the validity of using PAW core potentials created with LDA or PBE together with AM05 in VASP 5.1, we have performed all-electron calculations for the same set of solids using the RSPT (Ref. 59) code. To further compare the results given by the two codes, we have also performed LDA and PBE calculations with RSPT. The results are compared in Tables IV and V.

The RSPT code<sup>59</sup> is a full-potential linear muffin tin orbital (LMTO) code. Since it uses an efficient smaller basis set, it is fast compared to other all-electron codes, while the flexible basis, that has been specially built for every single solid, permits very well converged results. Our primary concern has been to construct a basis with small “leakage,” that is, to only keep as core orbitals the orbitals that do not significantly contribute to the density outside of the muffin tin spheres. We have thus, in most cases, used a larger number of valence orbitals than is needed for production runs. We

TABLE II. Lattice constants  $a_0$  (Å), ME, MAE, RMSE, and mean absolute relative error (MARE), obtained with the AM05, LDA, PBE, BLYP, and RPBE functionals, using VASP. The experimental (Exp) results are the same as used in Refs. 10 and 61.

Solid	Exp	AM05	LDA	PBE	BLYP	RPBE
Li	3.477	3.455	3.359	3.433	3.421	3.476
Na	4.225	4.212	4.052	4.201	4.210	4.295
Al	4.032	4.004	3.984	4.041	4.116	4.064
BN	3.616	3.605	3.583	3.627	3.647	3.646
BP	4.538	4.516	4.491	4.548	4.592	4.573
C	3.567	3.551	3.534	3.573	3.598	3.590
Si	5.430	5.431	5.403	5.467	5.532	5.499
SiC	4.358	4.350	4.330	4.377	4.411	4.398
$\beta$ -GaN	4.520	4.492	4.460	4.548	4.611	4.511
GaP	5.451	5.441	5.394	5.509	5.607	5.556
GaAs	5.648	5.672	5.611	5.755	5.871	5.812
LiF	4.010	4.039	3.908	4.065	4.084	4.146
LiCl	5.106	5.119	4.962	5.150	5.232	5.254
NaF	4.609	4.686	4.508	4.708	4.716	4.824
NaCl	5.595	5.686	5.466	5.702	5.763	5.847
MgO	4.207	4.232	4.168	4.259	4.281	4.302
Cu	3.603	3.565	3.523	3.637	3.711	3.682
Rh	3.798	3.773	3.757	3.833	3.905	3.857
Pd	3.881	3.872	3.844	3.946	4.034	3.984
Ag	4.069	4.054	4.002	4.150	4.262	4.215
ME	...	0.001	-0.070	0.039	0.093	0.090
MAE	...	0.025	0.070	0.046	0.100	0.091
RMSE	...	0.033	0.082	0.056	0.114	0.113
MARE	...	0.6%	1.6%	1.0%	2.2%	2.0%

TABLE III. Bulk moduli  $B_0$  (GPa), obtained with the AM05, LDA, PBE, BLYP, and RPBE functionals, using VASP. The experimental (Exp) results are the same as used in Refs. 10 and 61. For the materials marked with a star "\*", different experimental data are frequently quoted in the III-V literature, see Sec. IV C.

Solid	Exp	AM05	LDA	PBE	BLYP	RPBE
Li	13.0	13.0	15.1	13.7	13.7	13.1
Na	7.5	7.36	9.22	7.62	7.08	6.94
Al	79.4	83.9	81.4	75.2	54.9	73.7
BN	400*	378	394	365	350	353
BP	165	165	171	158	146	152
C	443	442	456	424	399	410
Si	99.2	90.2	93.6	86.4	77.0	83.1
SiC	225	217	224	208	194	201
$\beta$ -GaN	210*	181	196	166	152	237
GaP	88.7	80.2	87.0	74.3	64.3	69.4
GaAs	75.6	65.1	71.8	59.7	50.6	55.2
LiF	69.8	65.8	85.7	66.7	65.5	59.3
LiCl	35.4	30.3	40.4	31.2	28.9	27.3
NaF	51.4	43.2	60.1	44.5	44.3	38.3
NaCl	26.6	22.0	31.4	23.4	22.0	20.1
MgO	165	152	169	148	145	139
Cu	142	157	180	134	112	120
Rh	269	285	304	249	214	232
Pd	195	194	216	165	137	148
Ag	109	109	132	88.9	71.2	74.4
ME	...	-4.48	7.48	-14.1	-26.0	-17.9
MAE	...	8.10	10.7	14.2	26.1	20.5
RMSE	...	11.2	15.2	18.3	32.2	24.7
MARE	...	7.1%	10.8%	10.4%	18.7%	16.0%



TABLE IV. Lattice constants  $a_0$  (Å), obtained with AM05, LDA, and PBE, using VASP and RSPT. The AM05 VASP results are calculated using LDA and PBE PAW core potentials. As shown, the results are nearly identical. The AM05 values given in Tables II and III are the mean of the AM05 values obtained with LDA and PBE PAW core potentials. The two different codes also give similar results, showing that using PBE or LDA PAW core potentials for AM05 calculations in VASP is a valid approach.

Solid	AM05			LDA		PBE	
	VASP		RSPT	VASP	RSPT	VASP	RSPT
	LDA PAW	PBE PAW					
Li	3.4539	3.4559	3.456	3.359	3.362	3.433	3.434
Na	4.2124	4.2125	4.222	4.052	4.053	4.201	4.196
Al	4.0003	4.0076	4.008	3.984	3.986	4.041	4.043
BN	3.6026	3.6071	3.604	3.583	3.583	3.627	3.625
BP	4.5118	4.5203	4.520	4.491	4.495	4.548	4.553
C	3.5497	3.5529	3.551	3.534	3.534	3.573	3.573
Si	5.4306	5.4317	5.436	5.403	5.405	5.467	5.474
SiC	4.3491	4.3514	4.361	4.330	4.337	4.377	4.386
$\beta$ -GaN	4.4914	4.4921	4.506	4.460	4.465	4.548	4.553
GaP	5.4385	5.4435	5.457	5.394	5.405	5.509	5.518
GaAs	5.6689	5.6747	5.686	5.611	5.620	5.755	5.761
LiF	4.0364	4.0420	4.041	3.908	3.912	4.065	4.065
LiCl	5.1163	5.1223	5.114	4.962	4.966	5.150	5.149
NaF	4.6860	4.6866	4.685	4.508	4.507	4.708	4.692
NaCl	5.6844	5.6877	5.693	5.466	5.467	5.702	5.692
MgO	4.2352	4.2291	4.221	4.168	4.164	4.259	4.253
Cu	3.5641	3.5668	3.564	3.523	3.522	3.637	3.633
Rh	3.7729	3.7729	3.786	3.757	3.769	3.833	3.845
Pd	3.8713	3.8727	3.880	3.844	3.852	3.946	3.953
Ag	4.0538	4.0549	4.062	4.002	4.010	4.150	4.155
ME	-0.001	0.002	0.006	-0.070	-0.066	0.039	0.041
MAE	0.026	0.025	0.022	0.070	0.066	0.046	0.048
RMSE	0.033	0.033	0.033	0.082	0.079	0.056	0.056
MARE	0.6%	0.6%	0.5%	1.6%	1.5%	1.0%	1.1%

have used the same basis for a specific solid for all different functionals. For each of the seven volume points considered in the fits to the Murnaghan<sup>60</sup> equation of state, the muffin tin radius was varied so as to give a muffin tin sphere with a specific fraction of the cell volume. The volumes have been centered around the equilibrium volume given by the VASP calculations and spaced between  $\pm 3\%$  of the equilibrium lattice constants. The cells used have all been primitive. We used a  $24 \times 24 \times 24$   $k$ -point grid shifted by  $(1/2, 1/2, 1/2)$  for all solids and we used the tetrahedron method for integrating the  $k$  space. The Fourier grid was  $30 \times 30 \times 30$ .

Tables IV and V show that the differences using LDA or PBE core potentials in the VASP AM05 calculations are minute and that either set of results compares well with the all-electron RSPT calculations. Thus, if it is not possible to do both sets of AM05 calculations and use the mean, as we have done in this work, the choice between using LDA or PBE core potentials together with AM05, could be left as a practical consideration. For example, if LDA will also be used, LDA core potentials could be employed also for AM05.<sup>64</sup>

The comparison between RSPT and VASP LDA and PBE values also confirms that the VASP LDA and PBE core potentials almost always reproduce the all-electron lattice constants to within 0.1%–0.2%.

With RSPT, we have also confirmed that PBE and PW91 indeed give nearly identical results for lattice constants and bulk moduli of solids, something that led users to believe that PBE and PW91 would perform equally on all types of systems. However, this has been shown not to be the case (see Refs. 22 and 23).

In addition to the set of 20 solids, we next turn to a few additional metals: A heavy bcc metal (W), two heavy fcc elements (Pt and Au), and a light hcp metal (Be). Be is an hcp metal with experimental lattice constants  $a=2.29$  Å and  $c=1.567$  Å. Our results for  $(a,c)$  are the following: (2.232,1.58) for LDA, (2.264,1.58) for PBE, and (2.255,1.58) for AM05. The results for W, Pt, and Au are presented in Table VI. The PAW core potentials include scalar relativistic corrections and treat the semicore  $p$  states as valence. The number of valence electrons are thus 12 for W, 11 for Au, and 10 for Pt. It is well known that LDA is superior to PBE for these heavy elements (BLYP and RPBE both give results worse than PBE). AM05 yields lattice constants as well as bulk moduli in very good agreement with experimental data. The addition in AM05 of a surface model system to the LDA bulk region thus did not negatively affect the performance for this class of elements.

TABLE V. Bulk moduli  $B_0$  (GPa), obtained with AM05, LDA, and PBE, using VASP and RSPT. The AM05 VASP results are calculated using LDA and PBE PAW core potentials. As shown, the results are nearly identical. The two different codes also give similar results, showing that using PBE or LDA PAW core potentials for AM05 calculations in VASP is a valid approach.

Solid	AM05		LDA		PBE		
	VASP		VASP	RSPT	VASP	RSPT	
	LDA PAW	PBE PAW	LDA PAW		PBE PAW		
Li	13.01	12.99	13.2	15.1	15.0	13.7	13.9
Na	7.363	7.361	7.65	9.22	9.16	7.62	7.74
Al	84.08	83.63	86.2	81.4	82.5	75.2	77.1
BN	378.5	377.5	384	394	400	365	370
BP	165.1	164.3	168	171	174	158	160
C	442.5	441.4	450	456	465	424	431
Si	90.30	90.11	92.0	93.6	95.4	86.4	87.5
SiC	216.9	216.3	217	224	226	208	208
$\beta$ -GaN	180.6	180.5	183	196	199	166	170
GaP	80.31	80.13	81.1	87.0	88.2	74.3	75.1
GaAs	65.08	65.07	65.4	71.8	72.4	59.7	59.4
LiF	65.85	65.82	65.8	85.7	86.2	66.7	67.5
LiCl	30.31	30.25	30.7	40.4	41.0	31.2	31.9
NaF	43.27	43.08	42.4	60.1	60.4	44.5	45.6
NaCl	22.04	21.99	21.0	31.4	31.5	23.4	23.7
MgO	151.3	151.9	154	169	171	148	149
Cu	157.4	157.3	165	180	187	134	140
Rh	285.3	285.5	293	304	312	249	253
Pd	194.2	193.9	202	216	224	165	167
Ag	108.6	108.9	114	132	137	88.9	90.2
ME	-4.38	-4.59	-1.80	7.48	10.4	-14.1	-12.1
MAE	8.03	8.19	9.27	10.7	12.3	14.2	12.2
RMSE	11.2	11.3	11.9	15.2	18.4	18.3	16.2
MARE	7.1%	7.2%	8.1%	10.8%	11.8%	10.4%	9.3%

## IV. DISCUSSION

### A. AM05 is better than the best of LDA and PBE

For most realistic solid-state applications, such as size-converged calculations of defect formation energies and migration energies, the use of a hybrid functional is not practical because of the prohibitive computational cost. This is true, in particular, for investigating mixed systems (alloys or solid/molecular systems) at nonzero temperatures. Such calculations require both DFT based molecular dynamics (DFT-MD) and large supercells. For these demanding applications, a functional based only on quantities that are easily calculated, such as density and density derivatives, is currently paramount.

It could be argued that there is no need for new functionals for solid-state systems since the existing LDA and

PBE do yield good results. In particular, by selecting the best of LDA or PBE, for a specific system, the result can be further improved. However, such a choice between LDA and PBE is not possible if reliable experimental data is not available. Resorting to using either LDA or PBE depending on application is, therefore, not an approach with predictive power. The approach is particularly uncertain in mixed systems where LDA would be preferred for one component of the system and PBE for another. However, even when disregarding these shortcomings, Table VII shows that relying only on AM05, in general, is a better alternative than choosing the result of LDA or PBE that is closest to experiment. AM05 is significantly better for lattice constants, and, within the relevant precision of bulk moduli calculations, AM05 matches the results obtained when picking LDA or PBE depending on the system.

TABLE VI. VASP results for the heavy metals W, Pt, and Au: AM05 performs as well, or better, than LDA.

	$a_0$ (Å)				$B_0$ (GPa)			
	Exp	AM05	LDA	PBE	Exp	AM05	LDA	PBE
W	3.16	3.153	3.142	3.190	310	333	335	310
Pt	3.92	3.915	3.906	3.977	283	292	307	251
Au	4.065	4.076	4.053	4.161	166–171	164	183	137

TABLE VII. VASP results for lattice constants  $a_0$  (Å) and bulk moduli  $B_0$  (GPa), obtained with the best of LDA or PBE. The experimental (Exp) results are the same as used in Refs. 10 and 61. This choice between LDA and PBE is a common practice but the result is less accurate than using AM05.

Solid	$a_0$ (Å)			$B_0$ (GPa)		
	Exp	Best $a_0$	$a_0$ for best $B_0$	Exp	$B_0$ for best $a_0$	Best $B_0$
Li	3.477	3.433	3.433	13.0	13.7	13.7
Na	4.225	4.201	4.201	7.5	7.62	7.62
Al	4.032	4.041	3.984	79.4	75.2	81.4
BN	3.616	3.627	3.583	400	365	394
BP	4.538	4.548	4.491	165	158	171
C	3.567	3.573	3.534	443	424	456
Si	5.430	5.403	5.403	99.2	93.6	93.6
SiC	4.358	4.377	4.330	225	208	224
$\beta$ -GaN	4.520	4.548	4.460	210	166	196
GaP	5.451	5.394	5.394	88.7	87.0	87.0
GaAs	5.648	5.611	5.611	75.6	71.8	71.8
LiF	4.010	4.065	4.065	69.8	66.7	66.7
LiCl	5.106	5.150	5.150	35.4	31.2	31.2
NaF	4.609	4.708	4.708	51.4	44.5	44.5
NaCl	5.595	5.702	5.702	26.6	23.4	23.4
MgO	4.207	4.168	4.168	165	169	169
Cu	3.603	3.637	3.637	142	134	134
Rh	3.798	3.833	3.833	269	249	249
Pd	3.881	3.844	3.844	195	216	216
Ag	4.069	4.002	4.150	109	132	88.9
ME	...	0.006	-0.003	...	-6.67	-2.45
MAE	...	0.040	0.049	...	11.6	7.26
RMSE	...	0.048	0.053	...	16.6	9.79
MARE	...	0.9%	1.1%	...	8.0%	6.2%

## B. Differences between codes

Solid-state codes solve the KS equations using approximations that lead to less than perfect precision. When dealing with and comparing such small errors as those of AM05 and hybrids (see Table I), it is relevant to ask whether it is possible to determine which one is more accurate, and whether it is at all possible to conclude that another functional performs better or worse than AM05 (and hybrids) for the present solid-state systems.

Table V of Ref. 10 gives PBE lattice constants and bulk moduli for a subset of the 20 solids studied in this work, calculated using VASP, a full-potential LAPW code, and a Gaussian-type-orbital (GTO) code.

Our RSPT values compare extremely well with the PBE APW+lo values and the VASP values in Table V of Ref. 10, although it seems that the error bars of the RSPT calculations are slightly larger. Specifically, the RSPT lattice constants deviate by up to 0.3% from the VASP values and from the APW+lo values, whereas the difference between the VASP and APW+lo lattice constants is not exceeding 0.1%. It is still clear that all three codes are able to give highly converged results, and the results mutually support each other. In particular, for LDA and PBE, the VASP and RSPT statistical errors are practically identical. For the AM05 case, the use of LDA and PBE cores might slightly increase the VASP error bars, as indicated by the comparison of AM05 for RSPT and VASP. However, the error bars are still smaller than approximately 0.005 Å in the lattice constants and 3 GPa in the bulk

moduli. The same error bars are likely to apply to the HSE03 case, covered originally in Ref. 10. Hence, the difference in accuracy between the hybrids and AM05 cannot be resolved.

The small numerical error bars for the VASP 5.1 PAW calculations in this work and the work of Paier *et al.*<sup>10</sup> are not common to pseudopotential codes.<sup>22</sup> Comparing the data in Table I to data obtained with different codes and different types of pseudopotentials can thus not be done with the same small error bars, but the error bars should be expected to be significantly larger, if conventional pseudopotentials are applied.

The same conclusion holds for results obtained with all-electron GTO codes. The results in Table 5 of Ref. 10 (collected from Ref. 61) obtained with a GTO code do not compare as well with the LAPW results as the RSPT ones do.

## C. Differences to experimental data

The precision of the best codes and accuracy of the best functionals for solid-state calculations are now at a level where further improvement in accuracy likely cannot be distinguished without a better understanding of experimental error bars. Although not conclusive in itself, we note that the three best functionals in this study (AM05, HSE06, and PBE0) give the same accuracy within numerical uncertainties, indicating that the remaining disagreement might be a sign of experimental errors and not a consequence of functional accuracy.

An analysis of the VASP results in Table III reveals that

two solids alone account for a large part of the mean bulk moduli errors between AM05 and experimental data. The solids, with their respective errors in parenthesis, are GaN (−29.5 GPa) and BN (−22.0 GPa). Both errors are surprisingly large, at first suggesting that AM05 has a systematic problem with III-V nitrides. However, theoretical studies more specifically targeting these kinds of system quote other experimental values for the bulk modulus, namely, 190 GPa for GaN and 369 GPa for BN.<sup>62</sup> Using these values instead of the ones provided in Ref. 61 changes the AM05 errors for these two solids to the more expected −9 GPa for GaN and +9 GPa for BN. These two changes in experimental values yield a mean error (ME) of −1.93 GPa, a mean absolute error (MAE) of 6.45 GPa, a root mean square error (RMSE) of 8.19 GPa, and a mean absolute relative error (MARE) of 6.5% for AM05. Adapting this change in experimental values, the PBE0 and HSE06 results for these quantities would be slightly increased. This observation does not imply that AM05 has better accuracy for the bulk moduli than do the hybrids, but it does illustrate the difficulty in distinguishing between the performance of different functionals which have an accuracy at the level of AM05 and the hybrids. Although a comprehensive review of available experimental results is of interest, not only for GaN and BN, but for all solids, such an investigation is outside the scope of the present work.

A similar examination of the two solids with unusually large AM05 errors in lattice constants, NaF and NaCl, does not provide such a simple explanation. We should note that the AM05 lattice constants for these materials compare better to the experimental values than LDA and PBE, and that both hybrids' results, though closer, still have substantial deviations. Since RSPT confirms the VASP values, the PAW core potentials cannot be at fault. Considering these caveats, one can draw only few definite conclusions on the relative performance of the HSE06 and AM05 functionals. Generally, AM05 predicts slightly smaller lattice constants than the two hybrid functionals do. Interestingly, it also predicts smaller bulk moduli than HSE06, although the energy volume curvature is usually expected to increase at smaller volumes. Concomitantly, the average bulk moduli are slightly underestimated by AM05 compared to experiment. The underestimation is modest for the metals and semiconductors, but clearly increases towards more ionic compounds and becomes as large as 20% for the two most ionic compounds, NaF and NaCl. As already mentioned, these are the compounds with the largest errors in the AM05 lattice constants. The hybrid functionals performed very well for these two systems yielding a much larger—albeit still too small—curvature at the equilibrium volume. We note that these systems, as well as other ionic compounds, are largely exchange dominated in the sense of the adiabatic coupling theorem, i.e., the adiabatic coupling theorem and the GW method suggest that one should include a large fraction of the nonlocal exchange to account for the physics in these systems. In summary, ionic compounds are the only bulk systems where hybrid functionals might offer an advantage over the AM05 functional. The opposite applies to the metallic systems, where the AM05 functional seems to give an overall slightly better description than the hybrid functionals, in particular,

for the bulk moduli. More reliable error bars on the experimental values are required before further definite statements can be made.

## V. CONCLUSIONS

The subsystem functional AM05 is based on two exact reference systems: The uniform electron gas and the surface jellium. AM05 hence constitutes a systematic improvement upon LDA by adding terms depending on the gradient of the density while maintaining the exact exchange-correlation limit of LDA. The systematic improvement is confirmed numerically by our careful solid-state benchmarks (cf. Table I). Not only is AM05 found to be a significant improvement over LDA, but also for the studied quantities over other often-used functionals, e.g., PBE, BLYP, and RPBE. Within the high numerical precision of this study, AM05 is found to be as accurate as the most advanced hybrid functionals proposed to date, PBE0 and HSE06. The only exception are ionic systems, where AM05 clearly improves upon PBE, but still yields much too large volumes and much too small bulk moduli.

In further analysis, we find the performance of AM05, on average, to be even better than what a computational user would reach by choosing between LDA and PBE with guidance from experimental knowledge. Hence, AM05 provides a predictive power neither of these two functionals possess. Our comparison of results from different codes also shows that the level of precision available in modern codes, and the size of experimental errors for solid-state systems, will make it difficult to register a further improved functional for these applications without going far beyond the benchmark systems and properties studied in this work. Note that the AM05 construction was made solely on a theoretical and nonempirical basis. The excellent results thus strongly points to it having a sound theoretical basis. Furthermore, we would like to emphasize that the theoretical foundation of AM05 is fundamentally different from those of other available functionals (cf. Sec. II B). In studies where the calculated value is to be relied upon, in particular, when experimental data are either unavailable or have large uncertainties, more than one functional is often applied as a means to assess the accuracy. It is in such cases beneficial to employ functionals that are based on different fundamental principles.

The high speed and precision of the computer code VASP 5.1 makes it an excellent choice for functional assessment, expanding the possibilities of initial testing from simple properties for few atoms to include also large systems and DFT-MD. For the applications of this work, we found its PAW core potentials to be general enough to be interchangeable between different functionals, which saves the otherwise tedious work of generating pseudopotentials. Note, however, that this is a property pertaining to the PAW scheme and the implementation used by this code. Pseudopotentials generated according to other schemes are generally *not interchangeable* and doing so may severely affect the computational results.



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