

Comment on “Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces”

A recent Letter of Perdew, *et al.* [1] presents a new functional, PBEsol, intended for solid state and surface systems. It is based on a gradient expansion of the exchange energy and a final fit of the exchange-correlation (xc) energy to that of surface jellium. The former component “restoring the gradient expansion” is analyzed extensively and put forward as explanation for the excellent results, while the latter, which is a major component of the AM05 [2, 3] density functional, receives little attention. A brief comparison between AM05 and PBEsol is given in the supplementary material. The focus is on partial differences, e.g., how the AM05 exchange functional is far from reproducing the behavior of the gradient expansion and not on the integrated behavior of these two functionals. If results for AM05 and PBEsol were decidedly different, the indirect comparison would support the importance of an exchange functional with the features suggested by Perdew, *et al.* However, the most striking conclusion from a direct comparison of the two functionals is not how different they are, but, instead, that *AM05 and PBEsol yield identical results for a wide range of solids*. Hence, there is a problem in how the Letter uses the excellent results for lattice constants of solids as a main motivation for its central thesis, since these results are not unique to PBEsol.

Ropo, Kokko, and Vitos [4] found that surface energies from PBEsol and AM05 are very similar (Fig. 2 of Ref. 4) and that the two functionals give identical lattice constant and bulk modulus for all 19 tested magnetic and nonmagnetic 3d, 4d, and 5d metals. We find that identical results are not limited to transition metals but extend to all tested oxides and semiconductors (see Table I for a partial list). The level of agreement is unprecedented for two “different” density functionals and a well-grounded explanation of this behavior is important for the future development of density functional theory. PBEsol adopting the approach of AM05 in fitting the total xc energy to jellium surface energies appear as a possible explanation; in particular since it is this total xc sum, rather than the separate parts, that matters for applications [6]. However, Table SIV of the supplemental material presents a test for three solids that suggests that PBEsol obtains AM05-like results even before the fit is made. Should that hold generally true, an alternative explanation is that the exchange functional of PBEsol shares some fundamental similarity with that of AM05 despite the differences. The functionals may be more similar in practice than indicated by the supplemental material of Ref. 1 since they approximate different choices for the exchange energy density [5]. AM05 and PBEsol yield identical results for oxides, semiconductors, and transition metals. Until the relationship between AM05 and PBEsol is fully understood, the necessity of an exchange functional for

TABLE I: Equilibrium lattice constants a_0 (Å) and bulk moduli B_0 (GPa), obtained with AM05 [2] and PBEsol [1]. We use VASP5 and PBE PAW potentials, with the same settings as in Ref. [3], except for a tighter interval for the points used in the Murnaghan fit. Differences between codes can result in larger differences than those between PBEsol and AM05 [3]. The accuracy of VASP5 has been shown to be comparable to that of a full potential, all electron, LAPW code.

Solid	a_0 (Å)		B_0 (GPa)	
	AM05	PBEsol	AM05	PBEsol
BN	3.61	3.61	383	384
C	3.55	3.56	449	447
Si	5.43	5.43	92.3	93.3
GaAs	5.67	5.67	66.5	68.6
LiCl	5.12	5.06	30.7	35.0
MgO	4.23	4.22	154	157
α -Al ₂ O ₃	5.14	5.14	241	244
Na	4.21	4.17	7.45	7.86
Mo	3.13	3.14	284	283
Al	4.01	4.02	85.7	81.7
Cu	3.57	3.57	162	163
Pd	3.87	3.88	200	202

solids that “restores the gradient expansion” remains an open question.

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