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Gradient-dependent density functionals of the Perdew-Burke-Ernzerhof type for atoms, molecules, and solids

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One of the standard generalized-gradient approximations (GGAs) in use in modern electronic-structure theory [Perdew-Burke-Ernzerhof (PBE) GGA] and a recently proposed modification designed specifically for solids (PBEsol) are identified as particular members of a family of functionals taking their parameters from different properties of homogeneous or inhomogeneous electron liquids. Three further members of this family are constructed and tested, together with the original PBE and PBEsol, for atoms, molecules, and solids. We find that PBE, in spite of its popularity in solid-state physics and quantum chemistry, is not always the best performing member of the family and that PBEsol, in spite of having been constructed specifically for solids, is not the best for solids. The performance of GGAs for finite systems is found to sensitively depend on the choice of constraints stemming from infinite systems. Guidelines both for users and for developers of density functionals emerge from this work.

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Modern density-functional theory (DFT) (Refs. 1–3) owes its success and popularity largely to the availability of simple and reliable density functionals.[4] Among the most widely used such functionals are gradient-dependent approximations, such as the B88 exchange functional[5] or the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA) for exchange and correlation.[6] Although many other functionals are available, PBE is today the *de facto* standard for gradient-dependent functionals in solid-state physics, and, together with B88, in quantum chemistry. These gradient-dependent functionals also form the basis for the development of more sophisticated functionals of, e.g., the meta-GGA or hybrid type.

Given the importance of PBE both for countless practical applications of DFT, as well as for constructing more refined approximations, it is not surprising that over the years many variations of the basic PBE form have been developed.[7–11] Most of these are more empirical than the original construction in the sense that they include parameters fitted to test sets of selected systems and properties. None is uniformly better than the original PBE for all systems and properties. For more restricted classes of systems, however, it is not that hard to improve on PBE, as is illustrated by the recent proposal of PBEsol,[12] which was designed to improve on PBE specifically for solids. As this is still an extraordinary large and diverse class of systems, even an improvement “only” for solids is still a very major step forward, and consequently PBEsol is currently being implemented in many standard electronic-structure codes and intensely scrutinized.[13,14]

In the present Rapid Communication we point out that the step that led from PBE to PBEsol is, in fact, not unique, and allows several variations. We propose a family of functionals, which we call PBE(β,μ), of which both the original PBE and the original PBEsol are particular members and which includes at least three more alternatives. Each member of this family takes the value of the β and μ parameters from a different physical constraint, without statistical fitting to test sets of systems. Five PBE(β,μ) functionals are systematically tested for atoms, molecules, and solids and, within each class, for systems with physically and chemically different properties.

To begin, we recall that the original PBE functional has three parameters. One, β, appears in the correlation functional and was originally obtained by requiring that for weakly inhomogeneous high-density systems the second-order gradient expansion of the correlation energy was recovered.[15] Another, μ, appears in the exchange functional and in the original construction was obtained from requiring that the combined exchange and correlation functional predicts the correct linear response of bulk Jellium.[6] This latter requirement implies that $\mu=\pi^2\beta/3$. In PBE, this is used to fix μ once β is obtained from the correlation energy gradient expansion. (One of the alternatives we propose here is to invert this relation, using it to determine β once μ is obtained from the gradient expansion of the exchange energy.)

In PBEsol, β is determined instead by fitting to Jellium surface energies (JSEs) (a strategy proposed earlier by Armiento and Mattsson[16]), whereas μ is chosen such as to recover the second-order gradient expansion of the exchange functional. Our original motivation for reconsidering the choice of β and μ was that the JSEs used for obtaining β in PBEsol had themselves been calculated from the Tao-Perdew-Staroverov-Scuseria (TPSS) meta-GGA functional,[17] whose correlation energy in turn contains as an ingredient the original PBE correlation. It seems slightly inconsistent to us to employ in the construction of a functional designed to improve on PBE a fit to data obtained from a functional that itself contains PBE. In practice, however, this may be a rather purist objection as the TPSS JSEs are quite close to those obtained by other methods.[18,19]

A search for possibilities to avoid this small inconsistency, however, suggested a broader perspective on PBE and PBEsol: since the aim of PBEsol was to improve on PBE specifically for solids, and the gradient expansion is more relevant for the slowly varying densities of typical solids than it is for molecular densities, it seems promising to take *both* param-

TABLE I. Specification of the values of β and μ used in each of the investigated variants of PBE(β,μ).

	PBE(G_c,J_r)=PBE	PBE(J_s,G_x)=PBEsol	PBE(J_s,J_r) new	PBE(G_c,G_x) new	PBE(J_r,G_x) new	PBE(G_c,J_s) new
β	0.066725	0.046	0.046	0.066725	$3\mu/\pi^2$	0.066725
μ	$\pi^2\beta/3$	10/81	$\pi^2\beta/3$	10/81	10/81	n.a.

eters, β and μ, from the gradient expansion, without making any use of properties of Jellium. An additional advantage of extracting both parameters from the same source is that it enhances the chances of error compensation between the exchange and the correlation functional—an effect that is known to be behind the success of the local-density approximation and that has only partially been preserved by common GGAs.

Further exploration of the idea of a consistent (in the sense of coming from the same source) set of parameters suggests the alternative possibility to take both parameters, β and μ, from properties of Jellium, without making any use of gradient expansions. Specifically, we can determine β from JSEs and μ from the Jellium response function. *A priori*, this choice too could be expected to be good for solids, or at least for metals, as Jellium is the paradigm of metallic behavior in extended systems.

Table I presents a summary of the different variations of PBE and the corresponding values of β and μ. Our notation for the entire family of functionals is PBE(β,μ), where β and μ are replaced by $G_x(G_c)$ or $J_s(J_r)$, depending on whether the parameter has been obtained from the gradient expansion for exchange (correlation) or from Jellium surface (response properties). In this notation the original PBE becomes PBE(G_c,J_r), the original PBEsol becomes PBE(J_s,G_x), and the two alternatives just described read PBE(G_c,G_x) and PBE(J_s,J_r).

Table I also includes a further mixed choice in which β is determined from the Jellium response function and μ from the gradient expansion of the exchange energy, i.e., PBE(J_r,G_x). This is the functional alluded to above in connection with inversion of the relation $\mu=\pi^2\beta/3$. Mathematically, still another possibility would be to determine β from the gradient expansion of the correlation energy and μ, e.g., from fitting to JSEs, resulting in PBE(G_c,J_s), but the results from that fit are not available so we cannot test that option here.

We note that PBE and PBEsol contain a third parameter, κ, which is determined from the Lieb-Oxford (LO) bound.[20] Recently it has been suggested that the value of this parameter can be readjusted to possible tighter forms of the LO bound.[21,22] In the present work we do not change κ relative to the original PBE proposal in order not to mix the question of a possible tightening of the LO bound with that of consistent choices of the β and μ parameters. Future work should explore the consequences of combined changes of all three parameters. The proposal of Ref. 22, which in addition to values of parameters such as κ, β, and μ also changes the form of the PBE enhancement factor, is a step in this direction.

Restricting ourselves to exploring changes in only β and μ, we report in Tables II–IV the mean error defined as me $=\frac{1}{N}\Sigma_{i=1}^{N}(R_i-A_i)$, the mean absolute error (mae$=\frac{1}{N}\Sigma_{i=1}^{N}|R_i-A_i|$), and the mean absolute relative error [mare $=\frac{1}{N}\Sigma_{i=1}^{N}|(R_i-A_i)/R_i|$], where R_i is the reference (benchmark) value of the ith system and A_i is the corresponding approximate value for $N=26$ light atoms,[23] $N=14$ molecules,[24] and $N=13$ extended systems[25] chosen according to two requirements: (i) reliable benchmark data are available and (ii) different types of crystal structures and of chemical bonds are represented in the data set. In the following analysis, we focus mainly on the trends of the mare.

For atoms, we have performed all-electron calculations using the mesh-based (basis-set free) atomic code that is part of the SIESTA package.[26] We find that the original PBE predicts best ground-state energies. The alternative functional PBE(J_s,J_r), which takes both of its parameters from Jellium properties, comes second. This is rather unexpected as JSEs (used to obtain β) and bulk Jellium response functions (used to obtain μ) are maximally different from what one expects for atomic densities. Probably, this indicates a substantial error cancellation between exchange and correlation, made possible by taking both parameters from the same reference system.

TABLE II. Mean error (me), mean absolute error (mae), and mean absolute relative error (mare) (same labels are used in all tables) for ground-state energies (GSEs) E_0 (Ry) and ionization potentials (IPs) (Ry) for 26 light atoms (Ref. 23) ($Z=3-28$); relative percentage error for the H-atom GSE (RE$_\mathrm{H}$).

	PBE(β,μ)	G_c,J_r	J_s,G_x	J_s,J_r	G_c,G_x	J_r,G_x
	me	9.052	7.790	8.231	7.594	7.893
E_0	mae	9.354	9.210	9.232	9.207	9.211
	mare	0.00451	0.00627	0.00560	0.00662	0.00609
RE$_\mathrm{H}$	%	0.00191	2.26	1.43	2.65	2.03
	me	−0.245	−0.247	−0.244	−0.254	−0.243
IP	mae	0.258	0.260	0.257	0.266	0.257
	mare	0.368	0.370	0.367	0.380	0.366

TABLE III. The me, mae, and mare for atomization energies (AEs) (eV) and interatomic distances d(Å) for 14 small molecules (Ref. 24).

	PBE(β,μ)	G_c,J_r	J_s,G_x	J_s,J_r	G_c,G_x	J_r,G_x
AE	me	0.0452	0.566	0.532	0.458	0.615
	mae	0.299	0.614	0.584	0.616	0.647
	mare	0.0573	0.100	0.105	0.112	0.103
d	me	−0.0143	−0.0122	−0.0115	−0.0124	−0.00959
	mae	0.0231	0.0214	0.0201	0.0307	0.0223
	mare	0.0156	0.0152	0.0146	0.0204	0.0156

For atoms we also compared Koopman's theorem ionization potentials, i.e., the negative of the eigenvalue of the highest occupied Kohn-Sham orbital. Here original PBE, PBE(J_s,J_r) and the novel mixed choice PBE(J_r,G_x) perform very similarly, whereas PBEsol and PBE(G_c,G_x) are clearly worse. However, as ionization energies obtained from eigenvalues suffer from the self-interaction error and the resulting wrong asymptotics of the effective potentials, which is not addressed at all by changing the values of β and μ, a comparison of the performance of PBE(β,μ) for these quantities is less conclusive than that for total energies.

As a final test for atoms, we compared the error in the ground-state energy of the hydrogen atom. This error, arising in an $N=1$ electron system, is exclusively due to self-interaction. As the fifth line of Table II shows, the original PBE functional performs by far best of all tested variants, distantly followed by PBE(J_x,J_r). As all constraints investigated here stem from infinite systems, this illustrates a dramatic sensitivity of the performance of approximate functionals near $N=1$ to changing constraints arising from $N \to \infty$.

For molecules and solids, our calculations were performed with the SIESTA code,[26] employing norm-conserving Troullier-Martins pseudopotentials and a strictly localized TZP and DZP basis set for molecules and solids, respectively. Pseudopotentials for use with any of the PBE(β,μ) functionals were generated by employing the same functional also in the atomic all-electron calculations. Convergence with respect to the basis-set size was checked by repeating the molecular PBE calculations, as well as selected atomic and solid-state calculations, independently with a plane-wave code that is part of the CPMD package,[27] where convergence is controlled by a single parameter, the energy cutoff.

For molecules, original PBE=PBE(G_c,J_r) predicts best atomization energies, whereas the alternative PBE(J_s,J_r) predicts best interatomic distances. For both quantities PBEsol =PBE(J_s,G_x) comes second.

For solids, the original PBE functional is the worst of all tested members of the PBE(β,μ) family. Not surprisingly, PBEsol consistently outperforms PBE, but interestingly, it is itself outperformed by PBE(G_c,G_x) for lattice constants and bulk moduli and by the novel mixed choice PBE(J_r,G_x) for cohesive energies. Overall, the best performance is obtained from PBE(G_c,G_x).[28,29]

The present results suggest guidelines for the informed choice of density functionals and their construction: (i) the original PBE is not optimal for use in solid-state calculations and for molecular bond lengths. (ii) PBEsol, in spite of its name, is not the best PBE-type functional for bulk properties of solids, where PBE(G_c,G_x) performs much better. Surfaces require separate analysis. (iii) A consistent choice of parameters (in the sense of stemming from the same type of source) tends to benefit the performance of the functional: PBE(G_c,G_x) and PBE(J_s,J_r) are more often among the best or second-best performers than any of the other variants.[30] (iv) The good performance of PBE(G_c,G_x) for solids suggests that restoring the gradient expansion completely (for exchange and correlation, and not just partially, for exchange only, as in PBEsol) is beneficial for extended systems,

TABLE IV. The me, mae, and mare for lattice constants a(Å), bulk moduli B (GPa), and cohesive energies CE (eV) for 13 solids (Ref. 28).

	PBE(β,μ)	G_c,J_r	J_s,G_x	J_s,J_r	G_c,G_x	J_r,G_x
a	me	−0.129	−0.0722	−0.0881	−0.0692	−0.0724
	mae	0.129	0.0739	0.0890	0.0692	0.0753
	mare	0.0283	0.0165	0.0198	0.0153	0.0168
B	me	35.81	25.65	29.57	24.06	26.80
	mae	35.99	25.84	29.76	24.21	27.03
	mare	0.244	0.173	0.201	0.153	0.184
CE	me	−0.521	0.00831	−0.172	0.0136	−0.0136
	mae	0.555	0.282	0.280	0.288	0.278
	mare	0.117	0.0604	0.0659	0.0644	0.0598

whereas for finite systems (atoms and molecules) gradient expansions turns out to be a less important ingredient. (v) A common ingredient of functionals that perform well for finite systems is the Jellium response function, but there seems to be no systematic trend for the utility of the Jellium surface energy. (vi) Substituting a constraint arising from infinite systems by another, also arising from infinite systems, can have a dramatic effect even at the opposite end of the spectrum, for $N=1$.

Users of PBE and related functionals should thus be aware of the fact that within the functional form of PBE there is not one single choice of constraints that benefits all system types. A related aspect is that the original PBE has been used as ingredient in the development of recent meta-GGA functionals.[17,31] These constructions should also be reconsidered in view of the superior performance of some of the other PBE(β,μ) variants as more sophisticated high-level functionals should naturally be built using as ingredients the most reliable functionals from lower levels.

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[28] After completion of our calculations, we were informed by J. P. Perdew that in the supplementary EPAPS material of Ref. 12 the last table contains, in a column without label, four numbers that report lattice constants of solids obtained with the combination of parameters we here refer to as PBE(G_c,G_x). Consistent with what we find here, these numbers also indicate that PBE(G_c,G_x) is superior for solids to PBE(J_s,G_x)=PBEsol.

[29] We note that unlike lattice constants and bulk moduli, the cohesive energy of solids and the atomization energy of molecules depend on the atomic energies for which PBE(G_c,G_x) performs worst. For solid-state and molecular properties not depending on calculations for isolated atoms, the advantage of PBE(G_c,G_x) is more pronounced.

[30] This result conforms to the discussion of formal properties of the functionals sketched in the introduction: Of all possible variations of PBE(β,μ), only PBE(G_c,G_x) and PBE(J_s,J_r) take their parameters from the same source, thereby allowing the benefit of error cancellation to a larger extent than mixed choices. And of all possible alternatives to the original PBE, only PBE(G_c,G_x) and PBE(J_r,G_x) do not use TPSS JSEs that themselves were obtained using the original PBE functional within TPSS. We recognize that neither of these two criteria is very stringent, but we also note that taken together they uniquely select PBE(G_c,G_x) as the most appealing variant, independently of, but in agreement with, the empirical findings presented above.

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