Rehabilitation of the Perdew-Burke-Ernzerhof generalized gradient approximation for layered materials

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Rehabilitation of the PBE GGA for Layered Materials

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Abstract

The structural and energetic properties of layered materials present a challenge to density functional theory with common semilocal approximations to the exchange-correlation energy. By combining the most-widely used semilocal generalized gradient approximation (GGA), the Perdew–Burke–Ernzerhof (PBE) one, with the revised Vydrov–van Voorhis non-local correlation functional (rVV10), both excellent structural and energetic properties of 28 layered materials have been recovered with a judicious parameter selection. We term the resulting functional PBE+rVV10L, with the "L" indicating that it is for layered materials. Such a combination is not new, and only involves refitting a single global parameter. However, the resulting excellent accuracy suggests such a dispersion-corrected PBE for many aspects of theoretical studies on layered materials. For comparison, we also present the results for PBE+rVV10 where the parameter is determined by 22 interaction energies between molecules.

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Much interest has been attracted by the two-dimensional (2D) materials and their parent layered materials [1–4], since the experimental realization of graphene [5]. Layered materials present a huge challenge for density functional theory (DFT) [6], the current work-horse first-principles method. The difficulty comes from the coexistence of the weak van der Waals (vdW) interaction between the layers and the strong chemical bonding within the layer. The long-range vdW interaction is missing in commonly used semilocal density functionals, and the vdW-correction needed for layered materials seems weaker than that for molecular systems: most existing vdW density functionals that are good for molecular systems [7–15] overbind layered materials significantly [16–19]. It is not even easy to find a dispersion-corrected generalized gradient approximation (GGA) that is able to predict well both the geometric and energetic properties, i.e., the intra-layer lattice constant a, inter-layer lattice constant c, and inter-layer binding energy E_b [18, 19].

We have found a solution based on a meta-GGA, where we combined the strongly constrained and appropriately normed (SCAN) [20] meta-GGA and the revised Vydrov–van Voorhis non-local correlation functional (rVV10) [14, 15], with one parameter adjusted to the Ar_2 binding curve. The so-termed SCAN+rVV10 [21] functional is a versatile vdW density functional. It not only gives the best description for layered materials, but also excellently describes solids, molecular systems, and adsorption of benzene on metal surfaces. One important conceptual feature of SCAN+rVV10, distinguishing it from other popular vdW density functionals [22], is that the vdW non-local correlation functional is deliberately combined with a semilocal functional with a certain amount of intermediate-range vdW binding included from the exchange. Instead, previous work essentially sought a vdW-free exchange functional [7–15].

Inspired by this new concept, we revisit the possibility of a GGA-based vdW density functional for layered materials, and end up with a solution by combining the most-widely used Perdew-Burke-Ernzerhof (PBE) [23] GGA and rVV10. The resulting functional, termed PBE+rVV10L with the "L" denoting that it is for layered materials, achieves similar accuracy as SCAN+rVV10. PBE+rVV10L is not as versatile as its meta-GGA counterpart SCAN+rVV10. However, it is noticeably cheaper in computation, and numerically more stable thanks to the much simpler mathematical form of PBE. Besides, both rVV10 and PBE have been implemented in many ab-inito codes [38], and hence PBE+rVV10L provides a very handy solution for many problems related to layered materials. PBE+rVV10L is even better than the AM05-VV10sol functional [14, 18, 24], which is constructed in a similar way as here but with an additional parameter adjusted (for which a physically-sound justification was not provided). Combining PBE and rVV10 (or VV10) is new in the condensed matter physics community, but not in the quantum chemistry community where the PBE+VV10 has already been tested for molecular systems [25]. In this work, we will report the benchmarking results of this newly-proposed PBE+rVV10L, and will compare with the PBE+rVV10 for which the parameter is adjusted to the interaction energies of 22 molecular complexes (S22) [26, 27], as in the original VV10 [14] and rVV10 [15]. All calculations in this work were performed with the projector augmented wave (PAW) method [28] as implemented in the VASP code (version 5.4.1) [29–31]. The PAW pseudopotentials (version .52) for each element recommended by the VASP developers were employed (The standard pseudo-potential for W instead of the recommended "W_pv" was used because the latter suffers from ghost states). For more details, we refer to the Appendix in Ref. [21].

The rVV10 [14, 15] nonlocal correlation functional takes a form similar to that of the popular family of Rutgers-Chalmers vdW-DFs [7–12],

$$E_c^{nl} = \int d\boldsymbol{r} n(\boldsymbol{r})[\frac{\hbar}{2}\int d\boldsymbol{r'}\Phi(\boldsymbol{r},\boldsymbol{r'})n(\boldsymbol{r'}) + \beta]. \tag{1}$$

β vanishes for the Rutgers-Chalmers vdW-DFs, and the total exchange correlation functional reads

$$E_{xc} = E_{xc}^0 + E_c^{nl}. \tag{2}$$

Here $n(\boldsymbol{r})$ is the electron density, and $\Phi(\boldsymbol{r},\boldsymbol{r'})$ is the kernel describing the density-density interactions, E_{xc}^0 is the companying semilocal exchange correlation. To ensure zero E_c^{nl} for the uniform electron gas, $\beta = \frac{1}{32}(\frac{3}{b})^{\frac{3}{4}}$ in Hartree is required. Two empirical dimensionless parameters C and b appear in the kernel $\Phi(\boldsymbol{r},\boldsymbol{r'})$: C chosen for accurate $-C_6/R^6$ vdW interactions between molecules at large separation R, and b controlling the damping of E_c^{nl} at short range.

In the original form for VV10 and rVV10 [14, 15], the nonlocal correlation combines with the semilocal exchange-correlation functional [23, 32] $E_{xc}^0 = E_x^{rPW86} + E_c^{PBE}$, partly because the rPW86 exchange is nearly vdW-free [32]. For a semilocal E_{xc}^0, $C = 0.0093$ was generally recommended [14], and the b parameter was determined as 5.9 and 6.3 by fitting to the interaction energies of the S22 set [26, 27] for the original VV10 and rVV10. Increasing C or b generally results in a smaller vdW correction. Keeping the original semilocal part and

TABLE I. Layer–layer binding energy E_b in meV/Å^2, inter–layer lattice constant c in Å, and intra–layer lattice constant a in Å for 28 layered materials from SCAN+rVV10 [21] and PBE+rVV10L. The mean error (ME) and mean absolute error (MAE) are also given in the same units, and the mean relative error (MRE) and mean absolute relative errors (MARE) are given in percentage. The reference values for E_b are from RPA calculations, and from experiments for c and a [17, 19].

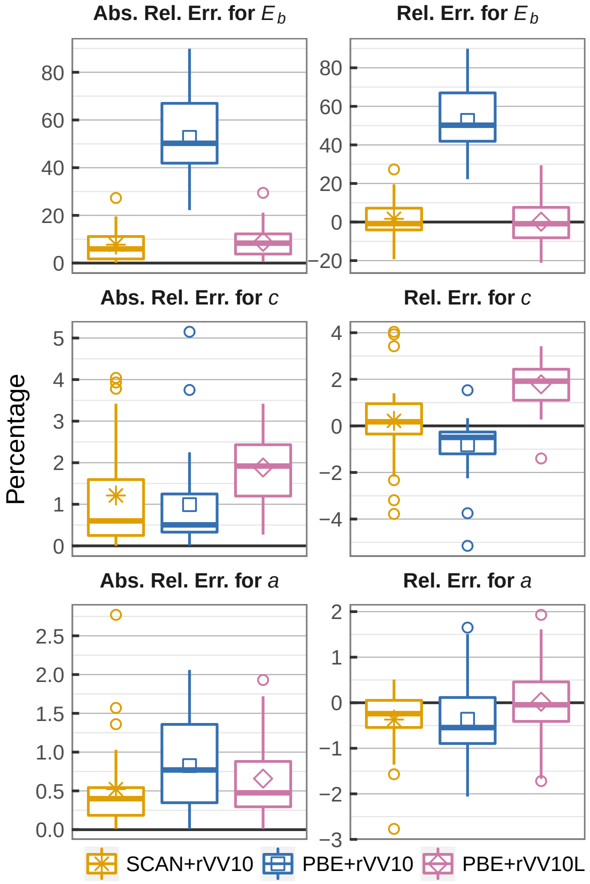
	Reference			SCAN+rVV10			PBE+rVV10L		
	E_b	c	a	E_b	c	a	E_b	c	a
TiS_2	18.88	5.71	3.41	18.90	5.68	3.40	18.04	5.79	3.39
$TiSe_2$	17.39	6.00	3.54	18.53	6.02	3.54	18.99	6.07	3.52
$TiTe_2$	19.76	6.50	3.78	19.74	6.59	3.75	22.65	6.55	3.75
VS_2	25.61	5.75	3.22	20.67	5.81	3.17	20.20	5.92	3.17
VSe_2	22.26	6.11	3.36	19.56	6.18	3.31	20.02	6.29	3.32
VTe_2	20.39	6.58	3.64	19.69	6.84	3.54	22.59	6.74	3.58
ZrS_2	16.98	5.81	3.66	15.95	5.79	3.67	15.12	5.93	3.66
$ZrSe_2$	18.53	6.13	3.77	16.54	6.12	3.78	16.32	6.24	3.77
$ZrTe_2$	16.34	6.66	3.95	19.53	6.67	3.97	21.15	6.69	3.93
NbS_2	17.58	17.91	3.33	20.20	18.11	3.33	19.78	18.42	3.33
$NbSe_2$	19.57	12.55	3.44	21.37	12.55	3.45	21.96	12.65	3.46
$NbTe_2$	23.03	6.61	3.68	21.83	6.88	3.64	23.51	6.84	3.67
MoS_2	20.53	12.30	3.16	19.89	12.28	3.16	19.24	12.57	3.17
$MoSe_2$	19.63	12.93	3.29	19.33	13.01	3.29	19.25	13.23	3.31
$MoTe_2$	20.80	13.97	3.52	20.45	14.14	3.50	21.40	14.13	3.53
$PdTe_2$	40.17	5.11	4.02	41.74	5.00	4.03	41.71	5.13	4.08
HfS_2	16.13	5.84	3.63	15.85	5.79	3.61	15.05	5.97	3.62
$HfSe_2$	17.09	6.16	3.75	16.10	6.14	3.73	15.80	6.27	3.74
$HfTe_2$	18.68	6.65	3.96	17.99	6.69	3.94	19.36	6.73	3.93
TaS_2	17.68	5.90	3.36	21.11	5.88	3.35	20.32	6.03	3.35
$TaSe_2$	19.44	6.27	3.48	20.67	6.27	3.46	20.82	6.38	3.47
WS_2	20.24	12.32	3.15	20.08	12.35	3.15	19.59	12.68	3.17
WSe_2	19.98	12.96	3.28	19.82	13.03	3.28	19.72	13.28	3.30
PtS_2	20.55	5.04	3.54	18.82	5.06	3.53	18.01	5.09	3.58
$PtSe_2$	19.05	5.08	3.73	19.02	5.25	3.71	19.79	5.01	3.79
Gra.	18.32	6.70	2.46	20.30	6.54	2.45	16.04	6.90	2.47
h-BN	14.49	6.69	2.51	18.45	6.48	2.50	14.43	6.85	2.51
PbO	20.25	5.00	3.96	22.93	4.81	3.98	17.95	5.08	4.04
ME				0.20	0.02	-0.01	-0.02	0.15	0.00
MAE				1.48	0.08	0.02	1.74	0.15	0.02
MRE				1.7	0.2	-0.4	0.2	1.8	0.0
MARE				7.7	1.2	0.5	8.9	1.9	0.7

value of C, a value $b = 9.15$ is required to fit the binding energies of 26 layered materials for both VV10 [18] and rVV10 [21], implying that layered materials require weaker vdW correction than molecular complexes. However, such a fitted b value leads to much worse performance for both the intra- and inter-layer lattice constants in layered materials, and also for solids [18]. Besides, $b = 9.3$ in rVV10 was proposed for the structural properties of water [33] where hydrogen bonding matters more, since the original VV10 and rVV10 overbind the seven hydrogen-bonded complexes from the S22 dataset [14, 15].

Changing the semilocal E_{xc}^0 to the SCAN meta-GGA [20] results in the versatile SCAN+rVV10 with $b = 15.7$ [21], and the SCAN+VV10 with $b = 14.1$ [34]. Setting E_{xc}^0 to the AM05 form [24] results in the AM05-VV10sol with $b = 10.25$ and $C = 10^{-6}$ [18], which works well for layered materials but not for S22. Note that a practically zero value for the C parameter was required by the fitting but not by chemistry. For PBE+VV10, $b = 6.2$ is determined by a fit to S22 [25]. In this work, we determine $b = 10.0$ for PBE+rVV10L by fitting to the inter-layer binding energies of 28 layered materials [17–19, 21], and $b = 6.6$ for PBE+rVV10 by fitting to S22. The b value for PBE+rVV10 is slightly larger than that for the original rVV10, in accordance with the slightly greater vdW binding from the PBE exchange than that from the rPW86 exchange [32]. The difference is related to the fact that the exchange enhancement factor of PBE is bounded by the Lieb-Oxford constraint as the reduced density gradient s increases [23], while the rPW86 enhancement factor diverges as $s^{0.4}$ [32]. The reference binding energies of the layered materials are not from experiments, but from the adiabatic-connection fluctuation-dissipation theorem within the random-phase approximation (RPA) [35–37], and are still the best available choice. Not expecting significant difference in the long-range asymptotic behavior due to different semilocal approximations, we keep the recommended C value of 0.0093 during the fitting in this work as was done for SCAN+rVV10 [21].

The lattice constants, both intra-layer a and inter-layer c, and the layer–layer binding energy E_b are the most fundamental quantities when one embarks on first-principles computation of layered materials. For benchmarking, we use the binding energies from RPA, and lattice constants from experiments as references [17, 19]. Until now, SCAN+rVV10 has been the only member of the “10-2-1” club for layered materials, simultaneously predicting with the mean absolute relative error $< 10\%$ for E_b, $< 2\%$ for c, and $< 1\%$ for a [21]. In Table I, we compare the results from PBE+rVV10L to those from SCAN+rVV10,

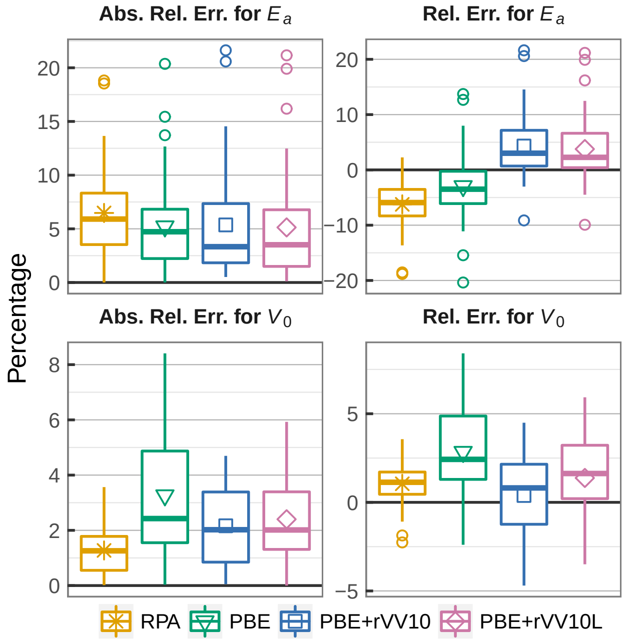
FIG. 1. (Color online) Box-plots for the absolute relative errors and relative errors of the inter-layer binding energies (E_b), inter- and intra-layer lattice constants (c and a) from SCAN+rVV10 [21], PBE+rVV10, and PBE+rVV10L, for 28 layered materials. The reference values are from RPA for the binding energy, and from experiment for the lattice constants [17, 19]. The Tukey box-plot used here summarizes the overall distribution of a set of data points: The bottom and the top of the box are the first (Q1) and third (Q3) quartiles (25% of data points lies below Q1, and another 25% above Q3); The band inside the box denotes the median; The circles if any denote outliers which lie further than $1.5*|Q3-Q1|$ away from the box; The vertical line extends from the minimum to the maximum, except for the outliers. Besides, we also denote the mean value with a shape inside the box.



and the reference values. PBE+rVV10L achieves excellent accuracy for both the structural and energetic properties by adjusting only the b parameter, which is not trivial as discussed above. PBE+rVV10L actually is comparable with SCAN+rVV10 for this class of materials, with a slightly overestimated layer-layer spacing. Nevertheless, PBE+rVV10L becomes a new member of the “10-2-1” club for layered materials. Considering the extremely simply mathematical form of both PBE and rVV10, and their wide availability in many scientific codes [38], PBE+rVV10L can be a very handy theoretical tool for studying layered material systems. It can also be used to prepare reasonably good initial (relaxed) structure and orbitals to accelerate the convergence of following SCAN+rVV10 calculations.

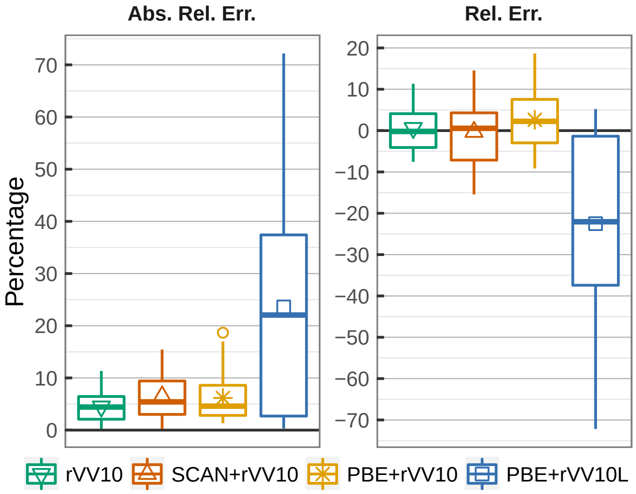
In Fig. 1, we summarize the absolute relative errors and relative errors for a, c and E_b from SCAN+rVV10, PBE+rVV10, and PBE+rVV10L. With a smaller b parameter, PBE+rVV10 overbinds the layered materials by about 50%, similar to the original rVV10, but the lattice constants are still reasonably accurate. Therefore, a b parameter between 6.6 and 10.0 may be empirically chosen in cases where the accuracy for the layer–layer binding energy is less relevant.

FIG. 2. (Color online) Box-plots for the absolute relative errors and relative errors of the atomization energies E_a, and the lattice equilibrium volumes V_0, from RPA, PBE, PBE+rVV10, and PBE+rVV10L for 50 solids, with respect to the experimental values. The RPA, PBE, and experimental values (after the zero-point correction) are from Refs. 39 and 40.



For solid systems, we further benchmark the performance of PBE+rVV10L and PBE+rVV10 using 50 solids compiled as in Ref. 21, which includes (i) 13 group–IV and III–V semiconductors, (ii) 5 insulators, (iii) 8 main-group metals, (iv) 3 ferromagnetic transition metals Fe, Co, and Ni, and (*v*) 21 other transition metals for which non-spin-polarized calculations were performed [39, 40]. We compared the mean relative errors and mean absolute errors for atomization energies and lattice volumes. The rVV10 correction decreases the mean absolute relative error for the atomization energies slightly for PBE, and the otherwise-underestimated atomization energies are slightly overestimated now with both PBE+rVV10 and PBE+rVV10L. However, atomization energy may not be a good choice to assess a semilocal functional [41]. It is well-known that PBE overestimates the lattice volume, with a mean absolute relative error over 3% as shown in Fig. 2. The attractive vdW correction slightly remedies this systematic overestimation by about 1%, and similar improvement over PBE by a vdW correction is also presented in recent works of Tao et al. [42, 43]. Overall, the structure and energetic properties for solids are not skewed by the rVV10 correction in both PBE+rVV10 and PBE+rVV10L.

FIG. 3. (Color online) Box-plots for the absolute relative errors and relative errors of the interaction energies from *r*VV10, SCAN+rVV10, PBE+rVV10, PBE+rVV10L, with respect to the CCSD(T) results [26, 27], for the molecular complexes in the S22 dataset.



We have calculated the PBE+rVV10 and PBE+rVV10L interaction energies of the 22 molecular complexes within the S22 dataset, which includes seven hydrogen-bonded, eight dispersion-bound, and seven mixed complexes. Fig. 3 compares the results to the rVV10 and SCAN+rVV10 results, and to the CCSD(T) reference [26, 27]. Similar to PBE+VV10 [25], the fitting of PBE+rVV10 is less accurate than the original rVV10 with the rPW86 exchange, and the mean absolute relative error of 6% (4.5% for rVV10). PBE+rVV10L with the b parameter fitted to layered materials significantly underbinds with a mean absolute relative error of 24% and a mean relative error of 22%. Nevertheless, PBE+rVV10L is noticeably better than AM05-VV10sol, whose mean absolute relative error is 36% [18]. Besides, PBE+rVV10L performs very well for the seven hydrogen-bonding complexes with a mean absolute relative error of only 2%. This indicates that PBE+rVV10L should be better than PBE+rVV10 for structural properties of water [33].

TABLE II. Adsorption energy E_{ad} and distance Δ_z between benzene and the (111) surface of Cu, Ag, and Au from PBE+rVV10 and PBE+rVV10L, compared with the SCAN+rVV10 results [21]. The data for the lowest-energy hcp30° configuration [44] is shown.

	PBE+rVV10		PBE+rVV10L		SCAN+rVV10	
	E_{ad} (eV)	Δ_z (Å)	E_{ad} (eV)	Δ_z (Å)	E_{ad} (eV)	Δ_z (Å)
Cu	0.84	2.88	0.52	3.05	0.74	2.93
Ag	0.74	3.02	0.46	3.18	0.68	3.02
Au	0.82	3.04	0.51	3.20	0.73	3.07

Finally, we benchmarked the performance of PBE+rVV10 and PBE+rVV10L with the adsorption of a benzene ring on Cu, Ag and Au (111) surfaces, systems which have been widely studied [44–49]. The SCAN+rVV10 results [21] agree very well with available experiments [50–55], and are chosen as reference here. In these systems, PBE+rVV10L is slightly worse than PBE+rVV10, underestimating the binding energy ΔE by about 0.2 eV and overestimating the distance Δ_z between benzene and metal surface by about 0.14 Å. PBE+rVV10 is better than PBE+rVV10L, and overbinds only slightly compared to SCAN+rVV10.

In conclusion, we provide here two set of parameters for the combination between PBE and rVV10. For systems involving molecules, the PBE+rVV10, where $b = 6.6$, gives a better prediction. For layered material systems (and perhaps also hydrogen-bonding systems), PBE+rVV10L, where $b = 10.0$, achieves the accuracy of the best dispersion-corrected semilocal density functional, so it is highly recommended. Values between these two may also be employed for specific systems. The PBE+VV10L and PBE+VV10 are not as versatile as the meta-GGA-level SCAN+rVV10 (where SCAN provides the intermediate-range vdW interaction), but they are very handy and computationally high-efficiency alternatives.

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