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Screened van der Waals correction to density functional theory for solids

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Lattice constant and cohesive energy are the basic properties in the design of materials and devices. However, due to neglect of long-range van der Waals (vdW) interactions, density functional approximations (DFAs) often yield unusually large errors for ionic solids and heavy metals. Here, we propose a model for the dynamically screened vdW correction, including the leading-order as well as higher-order contributions. The striking feature of this model is that important screening effects and higher-order contributions are properly considered, and that its contribution to the short-range part is removed by a novel damping function for the avoidance of double counting. As a result, the model dramatically reduces the error of the DFA-GGA in lattice constant and cohesive energy. We also find that the three-body interactions are small, due to the screening effects. These observations greatly improve our fundamental understanding of vdW interactions and enhance the applicability of efficient semilocal DFAs.

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Ionic solids and heavy metals are important materials representing two extremes in electric and mechanical properties. The former are hard insulators with large energy gaps but low fracture toughness, while the latter are soft conductors with zero energy gap and excellent ductility. Due to their wide applications, they have been extensively studied [1, 2]. Among the two different classes of materials, one thing is common. Both contain important van der Waals (vdW) interactions.

In the development of density functional approximations (DFAs) to the exchange-correlation energy [3–11], Kohn-Sham density functional theory has reached a high level of sophistication. In recent years, a large volume of literature studying lattice constant and cohesive energy with various DFAs has appeared. It was shown [12–15] that the local spin-density approximation (LSDA) tends to underestimate lattice constant and overestimate cohesive energy, while the generalized gradient approximation (GGA) tends to approach experimental values from the opposite direction. The reason is that, for bonded systems, LSDA tends to overestimate the short-range part arising from the electron density overlap [16], which often over-compensates for the long-range van der Waals interaction absent in semilocal DFAs [17]. As a result, LSDA yields too-short lattice constants [4], leading to too-large cohesive energy. However, the error of LSDA in cohesive energy is much less dramatic than that in molecular atomization energies, because the equilibrium separation between atoms in molecules is much smaller than that between atoms or ions in solids.

GGA [3] corrects the overbinding tendency of LSDA by raising the constant LSDA exchange enhancement factor through the incorporation of density gradients. The GGA exchange enhancement factor F_x is defined by $E_x[n] = \int d^3r \; n\epsilon_x^{\mathrm{unif}}(n)F_x(n, \nabla n)$, where $n(\mathbf{r})$ is the electron density. This gradient correction largely reduces the overbinding tendency of the LSDA [18]. Since there is no compensation for the missing long-range part, GGA tends to produce too-long lattice constants and too-small cohesive energies. The GGA correction to the short-range part of LSDA is successful in solids (although less so in molecules). This suggests that GGA for solids needs a full van der Waals correction [19–22].

Many van der Waals (vdW) corrections have been proposed [23–27]. Some of them only consider the dipole-dipole interaction. Since the equilibrium separation between molecules in the gas phase is larger than that in the solid phase, higher-order interactions are less significant in the gas phase, compared to the leading-order one. However, they become important in solids, as demonstrated by recent works [19, 28]. (For intramolecular interactions, higher-order terms are also important.) Thus there is great demand for the development of vdW corrections that include higher-order contributions.

In this work, we propose a vdW correction to DFA for solids, and combine it with the PBE GGA [3] to calculate lattice constants and cohesive energies of ionic solids and metals [1, 2]. In our formulation, the screening effect is accounted for via the modified Penn model [29] for the frequency-dependent dielectric function. Our goal is to provide a long-range vdW correction. This goal can be achieved with a damping function, which is designed to remove its contribution to the short-range part. Our calculations show that, with this screened vdW correction, the mean absolute error of GGA drops by a factor of three for lattice constant and a factor of two for cohesive energy, substantially improving the performance of GGA. We also find that the three-body contribution is very small, due to the dielectric screening. The structural phase transition from face-centered cubic (NaCl) to simple-cubic structure (CsCl) for Cs halides can be correctly predicted by the LSDA and all vdW-corrected DFA.

Formulation. The expression for the vdW correction to the DFA lattice constant can be derived by generalizing the formula of Ref. [30] valid for bcc (body-center cubic) structure of alkali metals to any cubic lattice. For this purpose, let us begin with the equation of state (EOS) of a solid $\epsilon(v) = \epsilon^{\rm DFA}(v) + \epsilon_{\rm vdW}(v)$, where v is the volume/atom, the first term on the right is the total energy/atom from DFA calculation, and the second term is the vdW contribution, which is absent in semilocal DFA. Then we expand the EOS around the DFA equilibrium volume v_0. For any cubic lattice, we have

$$\epsilon^{\rm DFA}(v) = \epsilon^{\rm DFA}(v_0) + (9p/2)B_0 a_0(\Delta a)^2, \qquad (1)$$

where $\Delta a = a - a_0$, with a_0 being the DFA equilibrium lattice constant, and $p = 1$ for simple cubic, 1/2 for bcc (body-center cubic), 1/4 for fcc (face-center cubic), and 1/8 for the rock salt (rs), diamond, and zinc-blende structure. B_0 is the bulk modulus defined by $B_0 = v_0 d^2\epsilon^{\rm DFA}(v)/dv^2|_{v=v_0}$. In the derivation of Eq. (1), we have used the fact that at the equilibrium state, the first derivative of the energy vanishes. This leads to $\epsilon_{\rm vdW}(v) = \epsilon_{\rm vdW}(v_0) + 3pa^2(d\epsilon_{\rm vdW}(v)/dv)|_{v=v_0}\Delta a + (9p/2)\Delta B a_0(\Delta a)^2$, where $\Delta B = v_0 d^2\epsilon^{\rm vdW}(v)/dv^2|_{v=v_0}$ is the vdW correction to the bulk modulus, and $d\epsilon_{\rm vdW}/dv = (1/3pa^2)d\epsilon_{\rm vdW}/da$.

The vdW correction to the lattice constant of DFA can be obtained by putting $\epsilon^{\rm DFA}(v)$ and $\epsilon_{\rm vdW}(v)$ together and minimizing the total energy. This immediately leads to the vdW correction, $\Delta a = a - a_0 = -(1/9a_0p)\epsilon'_{\rm vdW}(a_0)/(B_0 + \Delta B_0)$, where $\epsilon'_{\rm vdW}(a_0) = d\epsilon_{\rm vdW}/da|_{a_0}$. However, the PBE GGA tends to underestimate the bulk modulus, as seen from Table S4 of the supplemental material (SM) [31] (see discussion below). Adding the vdW correction (negative value) will slightly worsen the PBE bulk modulus. This term will be dropped. (If more accurate bulk moduli are used, the error will become smaller, as shown below). This leads to

$$\Delta a = a - a_0 = -\frac{1}{9a_0pB_0}\epsilon'_{\rm vdW}(a_0). \qquad (2)$$

The vdW correction to the cohesive energy is $\Delta\epsilon_{\rm coh} = \epsilon_{\rm coh} - \epsilon^{\rm DFA}_{\rm coh} = -\epsilon_{\rm vdW}(v)$. The quantities $\epsilon_{\rm vdW}(v)$ and $d\epsilon_{\rm vdW}/da$ can be calculated as follows. According to second-order perturbation theory, the vdW interaction between well-separated spherical objects is given by $\epsilon_{\rm vdW} = -C_6/d^6 - C_8/d^8 - C_{10}/d^{10}$, where d is the distance between two centers, and C_6, C_8 and C_{10} are the vdW coefficients [32, 33], measuring the dipole-dipole (C_6), dipole-quadrupole (C_8), as well as dipole-octupole and quadrupole-quadrupole (C_{10}) interactions.

In solids, the vdW interaction can be reduced by the screening effect from valence electrons [34]. For solids with the fcc or rs structure, the atoms or ions are so close to each other that a proper damping function must be applied to each term in the asymptotic formula $\epsilon_{\rm vdW}$ and its derivatives. However, a damping function is usually a step-like function of the distance d between atoms or ions. It rapidly goes to zero when d is smaller than the sum of the vdW radii, and approaches unity quickly when d is greater than the sum of the vdW radii. As such, its derivatives are highly sensitive to the choice of the vdW radius. To avoid this sensitivity problem but still fulfill the requirement that both the vdW energy and its derivatives must be finite everywhere, we calculate the vdW energy and its derivatives with respect to a first, and apply the damping function to each term in both the asymptotic expansion and its derivatives second. (This procedure will be explored in future work.) Thus the vdW interaction and its derivative per ion are given by

$$\epsilon_{\rm vdW} = \frac{-1}{2}\sum_{i,j,k} N_{ok}\left(\frac{C_6^{ij}}{d_{ok}^6} + \frac{C_8^{ij}}{d_{ok}^8} + \frac{C_{10}^{ij}}{d_{ok}^{10}}\right) f_d^{ij}(d_{ok}), \qquad (3)$$

$$\epsilon'_{\rm vdW} = \sum_{i,j,k} \frac{N_{ok}}{a}\left(\frac{3C_6^{ij}}{d_{ok}^6} + \frac{4C_8^{ij}}{d_{ok}^8} + \frac{5C_{10}^{ij}}{d_{ok}^{10}}\right) f_d^{ij}(d_{ok}), \qquad (4)$$

Here i, j represent positive (A) and negative (B) ions in ionic crystals and $i = j$ (i.e., A = B) in metals. k represents the k-th nearest neighbor shell of $N_{\rm ok}$ atoms or ions, and d_{ok} is the distance between the ion at o and those in the k-th shell. $f_d^{ij}(d_{ok})$is the damping function.

Several damping functions have been proposed [35–38]. A common feature of these damping functions is that they allow some amount of the long-range part to contribute to the binding energy when $d = d^{ij}_{\rm vdW}$. However, the Fermi-like damping function [37] was designed to cut off the short-range part of $-C_6/d^6$. Because $-C_6/d^6 - C_8/d^8 - C_{10}/d^{10}$ must diverge faster as $d \to 0$, a much stronger short-range cutoff is needed. To meet this consideration, we propose the following damping function

$$f_d(d/d_{\rm vdW}) = 1/(1+e^{-x})^6, \qquad x = c(d/d_{\rm vdW} - 1), \quad (5)$$

where d is the distance between ions, and $d_{\rm vdW}$ is the sum of the effective or vdW radii (see discussion below). Following the prescription of Wu and Yang [37], we determine c by requiring $f_d(d) = 0.99$ at $d = 1.2d_{\rm vdW}$. This gives $c = 32$. Figure S1 shows the comparison of our damping function with the Fermi-like one $f_d^{\rm Fermi}(d)$. From Fig. S1 we see that, as d approaches $d_{\rm vdW}$ or smaller than $d_{\rm vdW}$, $f_d(d)$ vanishes much faster than $f_d^{\rm Fermi}(d)$. At the short range $d = d_{\rm vdW} \approx d_{eq}$, $f_d(d) = 1/64$, which is much smaller than $f_d^{\rm Fermi}(d) = 1/2$.

Determination of vdW radius. It is important to cut off the vdW series at short range to avoid double counting, because the short-range part will be described by DFA in the DFA+vdW method. This cutoff can be performed with a proper vdW radius via our damping function of Eq. (5). Here we seek for a well-defined vdW radius. Given the static multipole polarizabilitiies of an atom or ion from high-level *ab initio* calculations, we can define the ionic vdW radii $r_l = [\alpha_l(0)]^{1/(2l+1)}$, where $l = 1, 2, 3$. For a classical conducting sphere of sharp radius R, we would find $r_1 = r_2 = r_3 = R$. For real atoms or ions with rapidly varying electron densities, we find that the sum of r_3 for a positive and a negative ion yields a much better approximation to the sum of Shannon's vdW radii [39], than does the sum of r_1 or r_2 (Table S4). This leads us to choose r_3 to define a vdW radius $R_{\rm vdW}$, to cut off the vdW series at short range, and therefore reduces the risk of overcorrecting GGA. Next, we observe that, for two classical conducting spheres A and B of radii $R^{\rm A}$ and $R^{\rm B}$, the vdW series may be summed to all orders [40], and the resummed series diverges when the separation between the centers approaches $R^{\rm A} + R^{\rm B}$, so the vdW radius for the short-range cutoff of a truncated vdW series (C_6,C_8,C_{10}) should be $R^i_{\rm vdW} = b\, r^i_3$, leading to the sum of the vdW radii $d^{ij}_{\rm vdW} = b_i r^i_3 + b_j r^j_3$, where $b > 1$ and is of order 1.

Screened vdW coefficients. The screened vdW coefficients between ions in a solid can be evaluated from [34, 41, 42]

$$C^{\rm sc}_{2m} = \frac{1}{2\pi} \sum_{l_1=1}^{m-2} \frac{(2(m-2)!}{(2l_1)!(2l_2)!} \int_0^\infty du\, \frac{\alpha^{\rm A}_{l_1}(iu)}{\epsilon^{\rm A}_1(iu)} \frac{\alpha^{\rm B}_{l_2}(iu)}{\epsilon^{\rm B}_1(iu)}. \quad (6)$$

Here $l_2 = m - l_1 - 1$, and $\alpha_l(iu)$ is the dynamic multipole polarizability, which can be modeled by [30, 43] $\alpha_l(iu) = [(2l+1)/4\pi d_l] \int_0^{R_l} dr\; 4\pi r^2 r^{2l-2} d^4_l \omega^2_l/(d^4_l \omega^2_l + u^2)$, where $l = 1$ (dipole), 2 (quadrupole), 3 (octupole), and $\omega_l = \omega_p \sqrt{l/(2l+1)}$, with $\omega_p = \sqrt{4\pi n}$ being the local plasmon frequency of the extended electron gas. Since $\alpha_l(iu)$ is not sensitive to the details of the electron density, it is evaluated from the Hartree-Fock densities [44]. The two parameters $R_l = [d_l \alpha_l(0)]^{1/(2l+1)}$ and d_l are determined by the low- and high-frequency limits [43] (see Table S5). Taking $R_3 = R_{\rm vdW}$ leads to $b = d_3^{1/7}$. The bulk dielectric function $\epsilon_1(iu)$ can be calculated as follows. For alkali metals, the dielectric function is given by $\epsilon_1(iu) = 1 + \bar{\omega}^2_p/u^2$, while for transition metals, it is given by [45, 46] $\epsilon_1(iu) = 1 + \bar{\omega}^2_{pf}/u^2 + \Omega^2/(u^2 + \omega^2_0)$. The second term is due to the free-electron intraband transition, while the third accounts for the bound-electron interband transition. Here $\bar{\omega}^2_{pf} = (1/m_{\rm opt})\bar{\omega}^2_p$ is the corrected bulk plasmon frequency, with $m_{\rm opt}$ being the optical mass [47]. The parameters $m_{\rm opt}$, ω_0 and Ω can be found from Ref. [48] (see Table S3).

The dielectric function of semiconductors and insulators can be simulated reasonably well with the modified Penn model [49]. (See SM [31] for detailed expression.) The inputs to the model are the average valence electron density obtained from $\bar{n} = N/a^3$, with N being the number of valence electrons in a conventional unit cell, bulk plasmon frequency $\omega_p = \sqrt{4\pi\bar{n}}$, and the effective energy gap ω_g. (Atomic units are used unless otherwise explicitly stated.) To make the model realistic, ω_g is determined by reproducing the correct static limit of the dielectric function $\epsilon_1(iu)$. We satisfy this condition with the Penn model [50], $\epsilon^{\rm Penn}_1(0) = 1 + (\bar{\omega}^2_p/\omega^2_g)[(1+\Delta^2)^{1/2} - \Delta]$, where $\Delta = \omega_g/4\epsilon_F$, with $\epsilon_F = (3\pi^2\bar{n})^{2/3}/2$ being the Fermi energy.

TABLE I: Statistical errors (in Å) of LSDA and PBE in comparison with our vdW correction and Grimme's D3 [26] to lattice constants and cohesive energies of ionic solids and metals. ME = mean error and MAE = mean absolute error.

	LSDA	PBE	PBE+vdW	PBE+D3
Lattice constant				
ME	-0.103	0.134	-0.008	-0.089
MAE	0.103	0.135	0.043	0.098
Cohesive energy				
ME	0.40	-0.18	-0.03	-0.04
MAE	0.40	0.18	0.08	0.07

Lattice constant. We first calculate the DFA lattice constants for 36 solids. All our calculations were performed with the all-electron, full-potential electronic structure code FHI-AIMS [51, 52] within the PBE exchange-correlation potential. For comparision, the LSDA lattice constants were also calculated with the same code. In our calculations, the so-called "tight" settings were used for all the elements. Second tier was used to ensure the convergence of the basis functions. Hartree potential and integration grid were also properly converged for the total energies of the solids and isolated atoms. The atomic zeroth-order regular approximation [51] was applied to treat relativistic effects. A uniformly distributed mesh of $24\times24\times24$ k-points was used to ensure converged Brillouin zone sampling for solids (see SM [31] for details). The deviations from experimental lattice constants at 0K, with zero-point energy (ZPE) effect removed, are summarized in Table I.

Next, we calculate the vdW correction with Eq. (2). The input bulk moduli B_0 can be calculated from EOS. Several models [53–55] for EOS have been proposed. These models should yield the same B_0. In this work, we calculate this quantity using the Birch-Murnaghan EOS [53]. We find that this model yields B_0 that agrees with the quadratic fitting within $1 \sim 2\%$. So, we believe that this is the true PBE bulk modulus (see Table S4 for detail). The vdW energy derivative is calculated from Eq. (4), and the screened coefficients are obtained from Eq. (6). The input static multipole polarizabilities and the static dielectric functions are taken from *ab initio* values in the literature. All the inputs are given in Tables S1-S3. The statistical error of the vdW correction to DFA lattice constant is displayed in Table I. For comparison, we have also calculated the lattice constants with the popular PBE+D3 (including the 3-body term) and PBE+TS methods proposed by Grimme *et al.* [26] (see Table I) and Tkatchenko and Scheffler (TS) [24] (Tables

S7), respectively.

From Table I, we observe that, without vdW correction, the PBE lattice constant is systematically too long. The error is even larger than that of LSDA. This suggests that there are strong vdW interactions in ionic solids and heavy metals. For solids that have strong vdW interaction, we observe that the lattice constant of LSDA is often more accurate than that of PBE, because the former tends to overestimate the short-range part, which can effectively compensate for the missing long-range vdW interaction, as pointed out above. However, with the vdW correction, the MAE of PBE drops from 0.135 Å to 0.043 Å, significantly improving the performance of PBE. The maximum deviation of PBE occurs for CsI in the rs structure, but this error drops from 0.225 Å to −0.043 Å with our vdW correction. The error is even smaller (MAE = 0.035 Å), if experimental bulk moduli are used (Table S7), supporting our formulation. We also observe from Table I that the dispersion D3 also improves upon PBE, but with an error (MAE = 0.098 Å) twice as large as our correction. The TS model significantly worsens the PBE values, with a huge MAE of 0.396 Å(see Table S7 for detail), which is even larger than that without correction. Our evaluation agrees well with that (MAE = 0.41 Å) of Kim *et al.* [56]. These authors have attributed the TS errors for ionic [56] and metallic [57] systems to the limitation [58] of the standard Hirshfeld partitioning. Much better results [56] were found from iterative Hirshfeld partitioning [58], but we could not access that correction to TS in FHI-aims. We have also applied the many-body dispersion (MBD) extension [59] of the TS model to these solids. But we have obtained only a few usefully converged results, as shown in Tables S7-S8. By fixing the convergence problem of MBD, remarkable results can be obtained [60].

Cohesive energy. Cohesive energy per atom is defined as the difference between the energy per unit formula in a solid and the total energy of constituent neutral atoms, divided by the number of ions or atoms in a unit formula. The DFA cohesive energies of 33 solids in the same set for lattice constant are calculated with the same code and parameter set. Due to the instability of CsCl, CsBr, and CsI with rock salt (rs) structure, their experimental cohesive energies are not available in the literature. Therefore, these three solids with rs structure have been excluded in our error analysis in cohesive energy. The statistical errors of the LSDA and PBE are given in Table I. The calculated individual cohesive energy and reference value can be found in Table S8. (The ZPE effect has been removed from experiments.) The vdW correction to cohesive energy can be obtained from Eq. (3), with the screened vdW coefficients calculated from Eq. (6). We have also calculated the cohesive energies with the PBE+D3 and PBE+TS methods. From Table I, we can see that the vdW correction is also important, reducing the error of PBE by a factor of two, a result similar to PBE+D3, but much better than PBE+TS (Table S8). This significantly improves the PBE description of energetics. The maximum deviation of PBE occurs for transition metal Au, but the error drops from −0.58 eV/atom to −0.27 eV/atom with our vdW correction. Our evaluation also agrees reasonably well with those of Kim *et al.* [56], in which they found that the original TS yields an MAE of 0.78 eV/atom, while the improved version TS-SCS produces an MAE of 0.38 eV/atom for 9 ionic solids.

TABLE II: Cohesive energies (in eV/atom) of CsCl, CsBr, and CsI with rock salt (NaCl) and simple cubic (CsCl) structures. Experimental values are taken from Ref. [61].

	Str	LSDA	PBE	PBE+vdW	PBE+D3	Expt
CsCl	rs	3.51	3.12	3.24	3.23	
	sc	3.54	3.07	3.25	3.24	3.25
CsBr	rs	3.28	2.91	3.03	3.03	
	sc	3.31	2.87	3.04	3.05	2.98
CsI	rs	3.01	2.66	2.79	2.74	
	sc	3.05	2.63	2.79	2.76	2.83

Structural phase transition of CsCl, CsBr, and CsI. Due to the increase of the volume of positive ion as well as negative ion from Li^+ to Cs^+ and from F^- to I^-, the most stable structure of CsCl, CsBr, and CsI is not the rs structure, as other family members take, but the less dense CsCl structure. To understand the details of this phenomenon, we calculate the cohesive energies of these halides in both rs and CsCl structures with the LSDA and PBE functionals. The results are displayed in Table II. From Table II, we observe that the LSDA cohesive energies of the CsCl structure are always larger than those of the rs structure for all three alkali halides, suggesting that the CsCl structure is a more stable structure. This is in perfect agreement with experiments.

However, PBE incorrectly predicts that the rs structure is more stable. When we add the screened vdW correction to PBE, the energy difference between the two structures becomes qualitatively correct, like LSDA, with the PBE+vdW cohesive energy in agreement with experiments. Recently, Zhang *et al.* [62] also found that, with a vdW correction to PBE, the right crystal structures could be predicted.

Higher-order contribution and screening effect. We have studied the higher-order contribution and dielectric screening on the lattice constant and cohesive energy of NaCl. For comparison, we first calculate the vdW coefficients with and without the screening. We show that the screening effect on the vdW coefficients is very important (Table S9). Then we calculate the lattice constant and cohesive energy. The results are given in Table S10. From Table S10 we see that, without higher-order contributions, the vdW correction will be underestimated by about 50%, while without the screening, the vdW effect will be overestimated by roughly the same. This suggests that simpler and less sophisticated methods often work well even for solids, due to error cancellation.

Screened three-body interactions. The three-body vdW interaction [63, 64] makes an additional contribution to the pair interaction of Eqs. (3)-(4). It can be evaluated with our model, as explained in SM [31]. Here we have evaluated the leading-order three-body contributions for NaCl. The results are given by Tables S9 and S11, respectively. From Tables S9 and S11, we observe that, due to the important screening effects, this contribution is very small and has been neglected in all our calculations.

In summary, we have proposed an accurate vdW correction to semilocal DFA for solids, and applied DFA+vdW to calculate the lattice constants and cohesive energies of ionic solids and metals. We find that, with the vdW correction, the performance of PBE can be significantly improved. This remarkable accuracy is largely due to the correct physics built into our model, such as (i) higher-order interactions involving C_8 and C_{10}, (ii) the screening effect, and (iii) strict separation between the short-range part and long-range part. To check our formulation, we have replaced the PBE bulk moduli with experimental values. We find that the results are even slightly better (Table S7). We further include the three-body interactions and find that this inclusion has a very small effect on two-body interactions, due to the screening, suggesting the robustness of the present model. We also evaluated the lattice constants and cohesive energies of these solids with the dispersion-corrected DFA methods PBE+D3 and PBE+TS. We find that, while PBE+D3 provides a fairly accurate description for these two quantities, the PBE+TS method worsens the PBE values [56, 57]. Our physics-motivated vdW correction should be applicable to some other semilocal functionals such as TPSS [4] as well, and thus sheds light on solid-state electronic structure calculations by moving them toward greater accuracy. Furthermore, our model has included many physical effects such as dielectric screening, higher-order interactions, and proper damping, without fitting any parameter to the predicted equilibrium properties of solids. This makes the model easily transferable from one system or lattice structure to another. We expect that our vdW correction should also improve the performance of PBE for other lattice structures very well.

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