uMBD: A Materials-Ready Dispersion Correction that Uniformly Treats Metallic, Ionic, Covalent, and van der Waals Bonding

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ABSTRACT. Materials design increasingly relies on first-principles calculations for screening important candidates and for understanding quantum mechanisms. Density functional theory (DFT) is by far the most popular first-principles approach due to its efficiency and accuracy. However, to accurately predict structures and thermodynamics, DFT must be paired with a van

der Waals (vdW) dispersion correction. Therefore, such corrections have been the subject of intense scrutiny in recent years. Despite significant successes in organic molecules, no existing model can adequately cover the full range of common materials, from metals to ionic solids, hampering the applications of DFT for modern problems such as battery design. Here, we introduce a universally optimized vdW-corrected DFT method that demonstrates an unbiased reliability for predicting molecular, layered, ionic, metallic, and hybrid materials without incurring a large computational overhead. We use our method to accurately predict the intercalation potentials of layered electrode materials of a Li-ion battery system – a problem for which the existing state-of-the-art methods fail. Thus, we envisage broad use of our method in the design of chemo-physical processes of new materials.

I. INTRODUCTION

Density functional theory (DFT) is currently able to provide reliable predictions for the physical and chemical properties of complex molecular and solid-state systems for a reasonable numerical cost. Nevertheless, the most common approximations to its key ingredient, the exchange-correlation (xc) functional, fail to describe nonlocal and long-range correlations often known as van der Waals (vdW) interactions. This shortcoming has led to a number of methodological advances usually referred to as vdW-corrected DFT methods (1-8). Among these, pairwise corrections such as those of Tkatchenko and Scheffler (TS) (1) and Grimme's D-series (2,9) are particularly popular because they are computationally inexpensive while retaining good accuracy. However, a further important advance was achieved in the form of the many-body dispersion (MBD) method (3), where collective effects beyond the pairwise approximation were

modeled through a set of quantum harmonic oscillators (QHO) that enable this approach to capture crucial many-body effects that are known as Dobson-B terms (10,11). Later, the connection between the MBD formalism and the random phase approximation (RPA) was elucidated (4), establishing this method, named MBD@rsSCS, as a computationally amenable RPA and the de facto reference method in the field. Despite such advances, the currently available methods still sometimes provide an imperfect description, particularly for systems in which the main interaction is of an ionic (5-7) or metallic (8,12) rather than van der Waals type.

Going beyond atom-wise theories, non-local van der Waals density functionals describe the van der Waals interaction by incorporating a nonlocal correlation functional with existing generalized gradient approximated (GGA) DFT or meta-GGA exchange. For example, SCAN+rVV10 (13) is known to have a balanced description of mid- and long-range dispersion by incorporating meta-GGA SCAN functional (14) with nonlocal rVV10 functional (15). At the GGA level, vdW-DF-cx (16) builds on successful predecessors [vdW-DF (17) and vdW-DF2 (18)] to provide uniform accuracy for both molecules and solids, via a more consistent description of exchange. Despite these advances, choosing a good functional for multiple types of systems remains challenging (19), and dispersion corrections sometimes make things worse.

Indeed, a “universally good” method should improve (or at least not degrade) the accuracy of the uncorrected DFT functional, which is particularly important when the strengths of the different types of interactions are of the same order of magnitude. One example is the intercalation of alkali metal ions into layered materials, where charge is transferred from the alkali metal to the layers, yielding a significant contribution of ionic bonding that coexists with vdW interactions. Accurate modeling of the intercalation energy is important to understand the de/intercalation process of a particular material; and more generally for reliable high-throughput

screening of materials (20,21) that are relevant for metal ion battery systems (22). In this case, a precise description can be obtained only if the vdW-corrected DFT accurately and unbiasedly treats (i) the ionic interactions between the intercalated ions and the layers, (ii) the vdW interactions between the layers, and (iii) the metallic interactions between the alkali atoms in the reference state. Unfortunately, most methods fail in at least one of these three cases.

Here, we present a universal many-body dispersion correction (namely, uMBD) that is able to treat the various types of interactions occurring in realistic systems on an equal footing. Using lithium cobalt oxide (LCO) – the most commonly used battery cathode material – as a prototypical example, we show that our method demonstrates the most balanced description of the structures and energetics of different materials involved in the de/lithiation process, enabling a reliable assessment of materials’ electrochemical performance from first-principles. We further demonstrate that our method has an unbiased accuracy for a wide range of type of interactions by performing exhaustive benchmark calculations for a wide range of systems – 22 molecular pairs, 63 crystals and 11 molecule-adsorbed surfaces. We then apply our method to predict the exfoliation behavior of 2D materials with the utmost reliability of the interlayer binding energies.

II. RESULTS AND DISCUSSION

1. Universal many-body dispersion correction

The key ingredients of our uMBD method are (i) a fractional ion (FI) scheme to obtain reliable atomic polarizabilities, and (ii) the use of smeared out dipoles to better account for the mid-range screening of fluctuating dipoles.

The coupled fluctuating dipole model introduced by Tkatchenko et al. (3) transformed the prediction of dispersion forces by including RPA-like effects in a computationally efficient method. Despite significant successes of this method for difficult problems (23,24), it is known to fail in describing ionic compounds (5-7) because it is based on “neutral”-atomic reference atoms. The FI approach (7) was thus introduced to enable an improved description of ionic systems by employing physically motivated polarizabilities for ions and atoms embedded in a system.

In parallel, it was proposed that mid-range screening is necessary to improve the accuracy of vdW corrections (8,12). As exemplified by the case of Ar dimer shown in Figure S1, the nonbonding correlation energy described using the DFT xc-functional (= DFT energy - Hartree-Fock energy) is considered to be proportional to the overlap of atomic wavefunction tails and thus decays exponentially as a function of the separation distance. However, the dispersive correlation energy decays algebraically, $\sim 1/r^6$. Thus, there is a “mid-range” in which these two effects compete, and the dispersive $1/r^6$ vdW correction must be attenuated to avoid the double counting of energies. The coupled fluctuating smeared-out dipole model (CFSDM) (8) provides a means to screen the interaction of the conventional MBD Hamiltonian in the mid-range and thus adequately compensates for the missing correlation energy of the original DFT (Figure S1). The importance of mid-range screening becomes critical particularly in metallic systems due to the diffuse nature of their atomic wavefunctions.

To achieve much improved descriptions of ionic and metallic systems, in this study, we combine these two methodological advances into the MBD@rsSCS framework. We simultaneously optimized two range-separation parameters a and β (see Equations [4] and [7] in the method section), by minimizing the error of the *S22 benchmark dataset* (25), leading to $a =$

0.88 and $\beta = 0.77$. Details about the FI and CFSDM schemes are summarized in the method section. The resulting method conserves better uniform accuracy than existing approaches across a range of important systems, as will be shown in the following discussion. Furthermore, it does so with similar cost and scaling as MBD.

2. Lithium intercalation to electrode materials

Discovery of new cathode materials for lithium-ion batteries (LIB) is being accelerated by computational materials design and screening (12,13). For high-voltage LIBs, lithiation potential (V) is an important property of the cathode oxide material (MO_2) that must be theoretically predicted in computational materials design, and it is calculated using the following formula (26,27):

$$\begin{aligned}
 V &= \frac{G(\text{Li}_{x+\Delta x}\text{MO}_2) - G(\text{Li}_x\text{MO}_2)}{\Delta x} - G(\text{Li}_{\text{bcc}}) \\
 &\cong \frac{E(\text{Li}_{x+\Delta x}\text{MO}_2) - E(\text{Li}_x\text{MO}_2)}{\Delta x} - E(\text{Li}_{\text{bcc}})
 \end{aligned} \tag{1}$$

where G denotes the free energy quantity that is often approximated as the DFT self-consistent field (SCF) energy, E . Thus, V is determined from the relative energetics of (i) metallic lithium (Li_{bcc}), (ii) the oxide cathode which is usually vdW layered (MO_2), and (iii) lithium intercalated oxide with ionic interactions inside due to the significant charge transfer between Li and the oxide layer (LiMO_2). This illustrates the importance of a balanced description within a single DFT methodology for the different types of interactions (ionic, dispersive, covalent) of the various materials.

As a prototypical example, we investigate the layered cobalt oxide, i.e., $M = \text{Co}$, which is the most widely used cathode material. **Figure 1** and **Table S1** show the comparison of different vdW correction methods in describing the structural properties of Li_{bcc} , CoO_2 , and LiCoO_2 . The conventional PBE significantly overestimates the interlayer spacing of CoO_2 by 25.4 %, whereas vdW corrections to the PBE resolve this problem.

However, the inclusion of vdW corrections severely degrades the description of Li_{bcc} . Both pairwise TS and previous many-body methods (MBD@rsSCS, MBD@rsSCS/FI) obtain unphysically compressed lattice parameters and grossly overestimated cohesive energies, whereas PBE without a vdW correction behaves much more reasonably. As reported in our previous study (8), Grimme's D3 method (2) demonstrates unphysical double energy minima in the equation of state of Li_{bcc} due to the use of a coordination-number dependent scaling scheme. Notably, among the vdW corrected methods considered here, only uMBD demonstrates accurate lattice parameters and cohesive energy (3.37 Å and 42.2 kcal/mol).

After lithium is intercalated into the CoO_2 , the interlayer interaction of LiCoO_2 is determined by both vdW interlayer interaction and ionic interaction between Li and the layer that originates from the electron transfer between Li and CoO_2 . Consequently, the layer spacing of LiCoO_2 is strongly underestimated if a pairwise vdW correction is included by the TS method (13.1 Å vs. 14.047 Å in experiment). On the other hand, both MBD@rsSCS and MBD@rsSCS/FI have negative atom-in-volume (AIM) polarizabilities that are not only unphysical but also lead to calculation crashes of long-range correlation energy in Equation [8] and as shown in **Table S1**. Again, among the considered vdW-corrected DFT methods, only uMBD obtains an accurate layer spacing (14.2 Å) by employing a smeared-out dipole potential. Thus, uMBD is the only

vdW correction method that reliably handles all three different materials: Li_{bcc} , CoO_2 and LiCoO_2 .

Based on its successful description of three different materials involved in the lithiation process, the uMBD method predicts the lithiation potential to be 4.0 V. This is in excellent agreement with the experimental potential of 3.9-4.6 V (28). Of the non-local functionals, SCAN+rVV10 predicts reasonable value of 4.5 V, which is consistent with the previous result of 4.1-4.7 V (29); but vdW-DF-cx gives 3.6 V, a more substantial underestimation than PBE (3.8 V).

In addition to cobalt oxides, we also validated the accuracy of the uMBD in other layered oxides and sulfides – vanadium oxide (V_2O_5), tin sulfide (SnS_2) and titanium sulfide (TiS_2). As shown in **Table S2**, uMBD predicts accurate average intercalation potential with a MAE of 0.14 V, which is far less than DFT and vdW-corrected DFT methods such as PBE (0.27 V) and TS (1.23 V), but also less than the state-of-art nonlocal functional approaches SCAN+rVV10 (0.17 V) and vdW-DF-cx (0.34 V).

3. Exhaustive benchmark of the new method

To unbiasedly demonstrate the reliability of our uMBD method in describing various interaction types, we perform an extensive test of uMBD on a wide range of systems. Our benchmark set includes the (i) *S22 set* consisting of 22 molecular pairs (25), (ii) *X23 set* consisting of 23 molecular crystals (30), (iii) *s-metal set* containing 12 alkali and alkaline-earth metals, (iv) *ionic-xtal set* containing 28 ionic crystals, and (v) *mol-ads set* containing 11 systems

of molecular adsorption on metallic surfaces, which are fully listed in the *Supplementary Materials* (**Figure S2-S3** and **Tables S3-S8**). We note that all of the benchmark sets use carefully obtained experimental data as reference values, except for the *S22 set* which uses the coupled cluster calculation results as reference values.

In **Figure 2**, we show the radar plots of mean absolute error (MAE) and mean absolute percentage error (MAPE) of each benchmark set which are also listed in **Figure S2** and **Table S3**.

uMBD shows reliable MAE (0.54 kcal/mol) for the *S22 set* – within chemical accuracy. This value is comparable with the original MBD@rsSCS method (0.61 kcal/mol) and the pairwise TS method (0.31 kcal/mol). These simple molecular systems can be described by only including the electronic compression effect, which is the property of the Dobson-A nonadditivity (10).

The *X23 set* highlights the significance of the Dobson-B nonadditivity contribution in condensed systems. uMBD shows a highly improved MAE (1.2 kcal/mol) for the *X23 set* that is comparable to that of MBD@rsSCS (1.1 kcal/mol) because both of these methods solve the many-body CF(S)DM Hamiltonian. The pairwise TS method, on the other hand, does not capture the many-body effect of Dobson-B nonadditivity and thus gives poor MAE (3.1 kcal/mol).

The *s-metal set* is a notable case where the previous methods based on the coupled fluctuating dipole model (CFDM) fail in the estimation of accurate physical properties. In contrast, uMBD based on the CFSDM shows exceptional accuracy in predicting cohesive energies (MAE = 3.7 kcal/mol), equilibrium volume (MAE = 1.3 Å³/atom) and bulk modulus (MAE = 4.3 GPa). By contrast, MBD@rsSCS significantly decreases the accuracy of the PBE (MAE = 3.1 kcal/mol), yielding an unphysical error of MAE = 16.4 kcal/mol. This failure of MBD@rsSCS is repeated

in the equilibrium volume (MAE = 5.3 Å³/atom of MBD@rsSCS vs. 1.8 Å³/atom of PBE) and bulk modulus (MAE = 8.0 GPa of MBD@rsSCS vs. 2.8 GPa of PBE) results.

As noted in our previous work (8), the inclusion of the interaction attenuation mechanism in the model is critical for describing the metallic system in which the screening starts by the large overlap of the diffuse charge densities in the mid-range. This is in stark contrast to the molecular systems in which well-confined charge distribution leads to a relatively small overlap of atomic charge densities at the interaction range.

Ionic crystals are another example in which uMBD improves results, and this is mostly ascribed to the success of FI over the Hirshfeld partitioning in accurately predicting the atomic polarizabilities (7). uMBD improves the prediction of atomization energy of the *ionic-xtal set*; MAE = 2.9 kcal/mol vs. 3.6 kcal/mol of PBE. On the other hand, the pairwise TS method gives incurable failure (MAE = 22.7 kcal/mol). The MBD@rsSCS gives mild improvement for the atomization energy of ionic crystals (MAE: 3.2 kcal/mol) but incurs unphysically negative AIM polarizabilities in some cases as shown in **Table S6**.

The *mod-ads* set is an example where diverse types of interactions (i.e., covalent, metallic and noncovalent) coexist. The uMBD method shows good agreement with the experimental values (MAE = 4.5 kcal/mol), which is far better than PBE (MAE = 9.7 kcal/mol) and is comparable with MBD@rsSCS (MAE = 4.5 kcal/mol). The absence of many-body screening in the pairwise TS methods is transferred to the adsorption systems in which the TS method shows systematic overestimation of the binding energy except for water bound to Pt (111) surface (MAE = 5.3 kcal/mol).

4. Comparison with nonlocal vdW density functionals

To compare the accuracy of the uMBD with the methods based on nonlocal functional approach, we also evaluated the accuracy of vdW-DF-cx and SCAN+rVV10 using our benchmark set.

In the *S22 set*, both vdW-DF-cx (MAE = 0.42 kcal/mol) and SCAN+rVV10 (MAE = 0.69 kcal/mol) show comparable accuracy with our uMBD method (MAE = 0.54 kcal/mol). SCAN+rVV10 has a slightly large MAE that is attributed to systematic overbinding of hydrogen-bonded complexes as shown in its mean signed error (MSE) for the hydrogen-bonded complexes (MSE = -1.5 kcal/mol vs. MSE = -0.8 kcal/mol by uMBD and MSE = -0.2 kcal/mol by vdW-DF-cx).

Both vdW-DF-cx (MAE = 2.1 kcal/mol) and SCAN+rVV10 (MAE = 2.1 kcal/mol) show mild MAEs for the *X23 set*. The vdW-DF-cx shows systematic overcohesion of molecular crystals with an MSE of -1.9 kcal/mol, which indicates stronger cohesion of molecular crystals than SCAN+rVV10 (MSE = -1.3 kcal/mol) and uMBD (MSE = -0.9 kcal/mol).

For the *s-metal set*, vdW-DF-cx shows the best performance (MAE = 1.6 kcal/mol), which is consistent with the previous work of Tran, *et al.* (19), where vdW-DF-cx is most reliable in strongly bound solids. SCAN+rVV10 (MAE = 3.5 kcal/mol) also shows comparable accuracy with uMBD (MAE = 3.7 kcal/mol) and PBE (MAE = 3.1 kcal/mol).

In the *ionic-xtal set*, vdW-DF-cx shows comparable MAE (3.3 kcal/mol) with uMBD (MAE = 2.9 kcal/mol), while SCAN+rVV10 has a slightly larger MAE (6.5 kcal/mol), mostly from alkaline earth oxides where SCAN+rVV10 exhibits 2 to 3-fold larger errors compared to uMBD

(MAE = 14.1 kcal/mol by SCAN+rVV10 vs. 4.9 kcal/mol by uMBD for alkaline earth oxides in *ionic-xtal set*).

The *mol-ads set* shows the most notable failure of vdW-DF-cx where it exhibits a larger MAE (11.9 kcal/mol) than PBE (MAE = 9.7 kcal/mol) and even no binding of benzene for the Ag (111) surface. On the other hand, SCAN+rVV10 shows mild MAE (6.9 kcal/mol), which is still slightly larger than uMBD (MAE = 4.5 kcal/mol).

The overall comparison of vdW-corrected DFT methods and nonlocal functionals shows that our method, uMBD, yields unbiased improvements for all of the benchmarked systems whose averages of MAEs and MAPEs from **Figure 2** are 2.6 kcal/mol and 10.9%, respectively, which is far better than the pairwise TS method (13.3 kcal/mol, 47.4 %) and many-body MBD@rsSCS (5.2 kcal/mol, 19.8 %) and MBD@rsSCS/FI (6.7 kcal/mol, 22.7 %) as well as the uncorrected DFT-PBE (6.3 kcal/mol, 38.7 %). It also shows improved performance compared with the nonlocal density functionals – vdW-DF-cx (3.9 kcal/mol, 23.3 %) and SCAN+rVV10 (4.0 kcal/mol, 13.3 %).

5. 2D materials exfoliation

Using our uMBD method, we predict the exfoliation properties of 2D materials. Despite its importance in various applications, the highly accurate determination of the exfoliation energy of 2D materials is still limited. This is because on the experimental side, temperature-programmed desorption (TPD) of a single-layer is not easily available; and on the theory side, the application of high-level wavefunction theory (e.g., coupled-cluster theory) is restricted in solids.

As representative examples of metallic, semiconducting, and insulating 2D materials, we calculated the interlayer binding energies of graphene, MoS₂, and *h*-BN, respectively (**Figure 3** and **Table S8**) by using our uMBD method and nonlocal vdW density functionals, vdW-DF-cx and SCAN+rVV10. All three methods similarly predict interlayer spacings within 0.10 Å that are also comparable with the experimental values. However, the predicted interlayer binding energies (ΔE_{bind}) are rather scattered.

For graphite, uMBD predicts ΔE_{bind} of 1.22 kcal/mol, which lies between ΔE_{bind} of SCAN+rVV10, 1.08 kcal/mol, and ΔE_{bind} of vdW-DF-cx, 1.49 kcal/mol. The SCAN+rVV10 and uMBD values reasonably agree with the adiabatic-connection fluctuation-dissipation theorem (ACFDT)-RPA result of 1.11 kcal/mol (31), while the value obtained by vdW-DF-cx is substantially overestimated. For MoS₂, the uMBD and the MBD@rsSCS similarly predict ΔE_{bind} of 0.81 kcal/mol and 0.88 kcal/mol, respectively, while vdW-DF-cx and SCAN+rVV10 predict slightly larger values of 1.19 kcal/mol and 1.04 kcal/mol, respectively. The uMBD mostly agrees with the ACFDT-RPA value of 0.68 kcal/mol (32). For *h*-BN, the uMBD value of 1.12 kcal/mol is smaller than the SCAN+rVV10 value of 1.22 kcal/mol and the vdW-DF-cx value of 1.52 kcal/mol. Therefore, the uMBD value is located closer to the ACFDT-RPA value of 0.90 kcal/mol (32) than the other two nonlocal density functional values.

Overall, uMBD is close to ACFDT-RPA but consistently slightly overbinds. However, ACFDT-RPA may underbind compared to reality, which would potentially make uMBD more accurate. In contrast, overbinding in vdW-DF-cx can be quite large, while errors in SCAN+rVV10 inconsistently lead to overbinding and underbinding in different 2D materials.

uMBD thus appears to be at least as good as the existing state-of-art, a property it shares with MBD@rsSCS/FI (33).

III. CONCLUSION

By learning from the successes and failures of existing approaches, we propose a universally optimal MBD method, namely, uMBD, which enables a balanced description of metallic, covalent, ionic and dispersive interactions in molecules and crystals within a unified vdW-corrected DFT framework. uMBD overcomes the reliability problems of the existing approaches by incorporating the theoretical basis of FI and CFSDM into the framework of MBD@rsSCS. The new approach reliably predicts the lithiation potential of a tested battery systems – a critical problem in modern material science for which most methods fail. More generally, uMBD conserves a better uniform accuracy over other methods across a wide range of systems, including the systems where dispersion corrections generally worsen the results. This feature seems to be unique amongst all the methods we tested. We anticipate that uMBD can be widely applied to investigate complex physics and chemistry in modern material science problems with a high reliability, e.g., for the applications of 2D materials, batteries, gas adsorptions, and heterogeneous catalysis. We speculate that its current successful performance may be further improved by optimizing the base functional. Furthermore, the coupling of uMBD with another base functional, e.g., hybrid functional, could provide a room for the accurate prediction of both the electronic structure and the energetics.

IV. MATERIALS AND METHODS

1. Coupled fluctuating smeared dipole model (CFSDM)

The original MBD@rsSCS calculates the correlation energy by solving the Hamiltonian of the coupled fluctuating dipole model (CFDM) (34), where oscillating point dipoles are coupled with the Coulomb potential W ;

$$H = -\frac{1}{2}\sum_i^N \nabla_i^2 + \frac{1}{2}\sum_i^N \omega_i^2 \chi_i^2 + \sum_i^N \omega_i \omega_j \sqrt{\tilde{\alpha}_i \tilde{\alpha}_j} \chi_i \mathcal{T}_{ij} \chi_j, \quad \mathcal{T}_{ij} = \nabla_{\mathbf{r}_i} \otimes \nabla_{\mathbf{r}_j} W(r_{ij}) \quad [2]$$

where χ_i is the displacement of the oscillating dipole centered at the atom i , and $\tilde{\alpha}_i$ and ω_i are the screened atomic polarizability and the characteristic frequency of the atom i , respectively. CFDM can also be understood as the set of point charges tethered at atom centers using harmonic springs—a small displacement of the point charge generates a point dipole, and thus can also be referred as a quantum shell model (QSM) (35) (**Figure S4A**).

We now generalize the QSM to make the shell have a finite size using the charge density, ρ (**Figure S4B**). Assuming that the shape of the shell is rigid upon a small displacement of the center of ρ from the atom center, the Hamiltonian in Equation [2] requires a replacement of W with the screened Coulomb potential, W_s , because the overlap of two charge densities screens the electrostatic interaction (36). When ρ follows a Gaussian distribution with the width of σ_i , the screened Coulomb potential is given by

$$W_s(r_{ij}) = \frac{\text{erf}(r_{ij}/\sigma_{ij})}{r_{ij}} \quad \text{where} \quad \sigma_{ij} = \sqrt{\sigma_i^2 + \sigma_j^2} \quad [3]$$

In previous work, Silvestrelli et al. suggested the use Wannier functions to estimate the screening length scale (37). However, Wannier function calculation is often computationally demanding, and demonstrates poor convergence without an appropriate initial guess (38). Instead, we simply relate (rs)SCS polarizability $\tilde{\alpha}_i$ to the screening length scale by introducing the scaling parameter a ;

$$\sigma_i = a \left(\sqrt{2/\pi} \tilde{\alpha}_i / 3 \right)^{1/3} \quad [4]$$

For a finite value of a , the dipolar interaction tensor of $\mathcal{T}_{ij}$ in Equation [2] becomes that of smeared-out dipoles, allowing us to call this model as the coupled fluctuating smeared dipole model (CFSDM) (8). In the limit of $a = 0$, CFSDM reduces to the original CFDM.

2. Fractionally ionic approach and range separation scheme

First, the polarizabilities of free-standing species (atom or ion) with nuclear charge Z and “integer” electron number M is designed as a two-Lorentzian model developed by Gould et al. (39):

$$\alpha_{Z,M}(i\omega) = \sum_{c=1,2} \frac{a_c(Z,M)}{\omega^2 + \Omega_c(Z,M)^2} \quad [5]$$

For infinitesimally small change to the potential, the response property of an atom (i.e., density response, polarizability, etc.) is piecewise linear in the electron number (7). Based on this piecewise linearity, the FI approach models the polarizability of a species with a “noninteger”

electron number N by interpolating the polarizabilities between the neighboring integer electron numbers $M = \lfloor N \rfloor$ and $M + 1$:

$$\alpha_{Z,N}(i\omega) = f\alpha_{Z,M+1}(i\omega) + (1 - f)\alpha_{Z,M}(i\omega)$$

where $f = N - M$.

To integrate CFSDM into the MBD@rsSCS framework, we apply the range separation scheme. For the short-range part, we solve the range-separated self-consistent screening (rsSCS) equation to obtain atomic polarizability $\tilde{\alpha}_i$ by replacing the Hirschfeld partitioning to the FI scheme (7), and by using the reoptimized parameter β in the range-separation function given by

$$f(r_{ij}) = \frac{1}{1 + \exp[-d(r_{ij}/S_{\text{vdW},ij} - 1)]} \quad [7]$$

where $S_{\text{vdW},ij} = \beta(R_{\text{vdW}}^i + R_{\text{vdW}}^j)$ is a scaled distance of the vdW radii (R_{vdW}), and $d = 6.0$.

After obtaining the rsSCS atomic polarizability of $\tilde{\alpha}_i$, we compute the long-range dipolar interaction tensor of the CFSDM Hamiltonian,

$$\mathcal{T}_{\text{LR},ij} = f(r_{ij})\nabla_{\mathbf{r}_i} \otimes \nabla_{\mathbf{r}_j} W_s(r_{ij}) \quad [8]$$

More details about the computational procedures can be obtained from the previous publications about MBD@rsSCS (4) or MBD@rsSCS/FI (7).

3. Computational details

We assessed the performance of PBE, PBE-D3, PBE-TS, PBE-TS/HI (5,6), PBE-TS+SCS (3) and PBE+MBD@rsSCS/FI using the Vienna *ab initio* simulation package (VASP) 5.4.1 (40-42), vdW-DF-cx using VASP 5.3.3 with an unofficial patch by Björkman (43), and SCAN+rVV10 using VASP 5.4.4. MBD@rsSCS and uMBD calculations were performed using our own external code for many-body dispersion methods with the dispersion coefficients and polarizabilities obtained from the Tkatchenko-Scheffler (TS) and fractionally ionic (FI) approaches in VASP. The FI method is available as a patch for VASP, by request to the authors of publication (7). Implementation of our external uMBD code into VASP is also underway. We used the pseudopotentials constructed by the projector augmented-wave (PAW) method (44). Optimization and single point calculations were performed with the kinetic energy cutoff of 900 eV, and the density of k-mesh was set to $0.15 \text{ \AA}^{-1}$ for periodic systems and only Γ -point was used for nonperiodic systems. In calculations of the systems related with Li intercalation, the kinetic energy cutoff was set to be 520 eV, and the density of k-mesh was set to be 1000 k-points/atom. Spin-polarized DFT was employed for calculations of atomization, cohesive energy and lithiation. In case of Li-intercalated compounds, Hubbard U correction (DFT+ U) was employed for Co and V of which U value was 3.32 eV (21) and 3.25 eV (45), respectively. Since force evaluation is not yet available for uMBD, optimal lattice parameters were obtained by the series of single-point calculations of PBE-optimized structures during the lattice expansion for the calculation of the layered materials and the intercalation processes based on all of the tested methods in this work. The calculation of an argon dimer was performed by using the NWChem 6.1 (46) with def2-qzvpp basis set (47).

Figure 1. Intercalation of lithium ion into an electrode material. Physical properties – lattice parameter c and cohesive energy E_{coh} – of different materials, **(A)** Li, **(B)** CoO₂, and **(C)** LiCoO₂, are calculated and compared to the experimental values (black line). These determine the intercalation process, resulting in the **(D)** lithium intercalation potential, Φ , of the CoO₂ cathode

material. uMBD shows balanced descriptions of different materials with metallic, vdW dispersive, and ionic interactions, resulting in an excellent agreement of Φ with the experimental value (the range shown in magenta).

A Mean absolute error (kcal/mol) **B Mean percentage absolute error (%)**

Figure. 2. Universally optimal description of the uMBD of diverse interactions. (A) Mean absolute errors (MAEs, in kcal/mol) and (B) mean absolute percentage errors (MAPEs, in %) of uMBD (navy) are compared to those for the bare PBE (orange), other vdW correction methods of TS (red) and MBD@rsSCS (cyan) and nonlocal density functionals, vdW-DF-cx (green) and SCAN+rVV10 (blue). The benchmark sets include systems with diverse interactions of molecular (*S22*), molecular crystal (*X23*), metallic (*s-metal*), ionic (*ionic-xtal*), and hybrid materials (*mol-ads*). Numbers in parentheses are the number of structures in the corresponding benchmark sets which are listed and illustrated in the Supplementary Materials.

Figure. 3. Binding properties of 2D materials. Interlayer binding energies (E_{bind}) and interlayer distances (d) of (A) AB-stacked graphite, (B) 2H-MoS₂, and (C) AA'-stacked *h*-BN of uMBD are compared to those obtained by the bare PBE and other standard methods based on nonlocal

correlation functionals (vdW-DF-cx and SCAN+rVV10). As reference data (31,32), the ACFDT-RPA results (black dashed line) and experimental values (magenta line) are also shown.

ASSOCIATED CONTENT

Supplementary Materials. Supplementary figures and tables are included as follows.

Fig. S1. Dissociation energy curve of an argon dimer

Fig. S2. The structures of benchmarked systems

Fig. S3. Scattered plot for the benchmark calculation of various density functional dispersion corrections

Fig. S4. Point dipole and smeared-out dipole model.

Table S1. Intercalation potential of a lithium ion between cobalt oxide (CoO_2) layers

Table S2. Properties of Li-intercalated compounds

Table S3. List of benchmark systems

Table S4. Benchmark test for various systems

Table S5. Benchmark test for *s-metal set*.

Table S6. Benchmark test for *ionic-xtal set*.

Table S7. Benchmark test for *mol-ads set*.

Table S8. Benchmark test for layered materials.

AUTHOR INFORMATION

Notes

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Supplementary Material

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Figure S1. Dissociation energy curve of an argon dimer. (Top) The PBE exchange-correlation and HF exchange energy curves are shown in red and black, respectively. The difference energy of PBE and HF is shown in green with its exponential fit $E = -A \exp(-Bx)$ in blue. (Bottom) The CFDM and CFSDM energy curves in red and black, respectively. The difference energy of CFDM and CFSDM is shown in green with its exponential fit $E = -C \exp(-Dx)$ in blue.

S22 set

Figure S2. The structures of benchmarked systems. The systems for which the benchmark calculations were performed: 22 molecular pairs (*S22 set*), 23 organic crystals (*X23 set*), 12 s-valence metals (*s-metal set*), 28 ionic crystals (*ionic-xtal set*), 11 adsorption systems (*mol-ads set*) and 3 layered materials.

X23 set

Figure S2 (cont'd). The structures of benchmarked systems. The systems for which the benchmark calculations were performed: 22 molecular pairs (*S22 set*), 23 organic crystals (*X23 set*), 12 s-valence metals (*s-metal set*), 28 ionic crystals (*ionic-xtal set*), 11 adsorption systems (*mol-ads set*) and 3 layered materials.

s-metal set

Body-centered cubic
Li, Na, K, Rb, Cs, Ba

Hexagonal closest packed
Be, Mg

Face-centered cubic
Ca, Sr

ionic-xtal set

NaCl structure
LiF, LiCl, LiBr, Lil, NaH, NaF, NaCl, NaBr, NaI,
KH, KF, KCl, KBr, KI, RbH, RbF, RbCl, RbBr, RbI,
CsH, CsF, MgO, CaO, SrO, BaO

CsCl structure
CsCl, CsBr, CsI

Figure S2 (cont'd). The structures of benchmarked systems. The systems for which the benchmark calculations were performed: 22 molecular pairs (*S22 set*), 23 organic crystals (*X23 set*), 12 s-valence metals (*s-metal set*), 28 ionic crystals (*ionic-xtal set*), 11 adsorption systems (*mol-ads set*) and 3 layered materials.

Layered materials

Figure S2 (cont'd). The structures of benchmarked systems. The systems for which the benchmark calculations were performed: 22 molecular pairs (*S22 set*), 23 organic crystals (*X23 set*), 12 s-valence metals (*s-metal set*), 28 ionic crystals (*ionic-xtal set*), 11 adsorption systems (*mol-ads set*) and 3 layered materials.

Figure S3. Scattered plot for the benchmark calculation of various density functional dispersion corrections. (A) Binding energy of 22 molecular pairs in *S22 set*. **(B)** Sublimation energy of 23 molecular crystals in *X23 set*. **(C)** Equilibrium volume, **(D)** cohesive energy, **(E)** bulk modulus of *s-metal set*.

Figure S3 (cont'd). Scattered plot for the benchmark calculation of various density functional dispersion corrections. (F) Lattice parameter and (G) atomization energy of 28 *ionic-xtal* set. (H) Adsorption energy of 11 pairs of molecules on metal surfaces in *mol-ads* set.

Figure S4. Point dipole and smeared-out dipole model. (A) Coupled fluctuating dipole model (CFDM) with point dipoles. (B) Coupled fluctuating smeared-out dipole model (CFSDM) where shell charges are described as the finite-width Gaussian-type dipoles.

Table S1. Intercalation potential of a lithium ion between cobalt oxide (CoO₂) layers. The physical properties – lattice parameters a and c , cohesive energy E_{coh} and bulk modulus B – of bulk structures related to the intercalation process, and the intercalation potential, Φ , of a lithium ion into layered CoO₂ based on PBE and PBE + various van der Waals corrected DFT methods in comparison with nonlocal density functional calculations (S1,S2).

	Li (<i>bcc</i>)			CoO₂ ($R\bar{3}m$)		LiCoO₂		Φ (V)
	a (Å)	E_{coh} (eV)	B (GPa)	c (Å)	%Error	c (Å)	%Error	
Experiment	3.449 ^a	1.668 ^a	13.3 ^a	13.44 ^b		14.047 ^b		3.9-4.6 ^c
PBE	3.437	1.621	15.2	16.9	25.4	14.1	0.5	3.8
TS	2.615	3.866	85.7	13.8	2.5	13.1	6.7	3.3
MBD@rsSCS	3.157	2.838	24.9	14.4	7.2	crashed		-
MBD@rsSCS/FI	3.224	2.928	15.3	14.7	9.7	crashed		-
vdW-DF-cx	3.453	1.662	13.4	13.5	0.6	13.8	1.8	3.6
SCAN+rVV10	3.454	1.634	13.4	12.8	4.8	13.8	1.8	4.5
uMBD	3.367	1.829	17.2	14.7	9.4	14.2	1.2	4.0

^a Ref (S3)

^b Ref (S4)

^c Ref (S5)

Table S2. Properties of Li-intercalated compounds. Average intercalation potential of a lithium ion between oxides and sulfides and lattice parameters of delithiated and lithiated compounds in comparison with experimental values of Ref. (S4). All in-plane lattice parameters were fixed with experimental values, and the lattice structures were minimized at PBE-level.

Average intercalation potential (V)							
System	Space group	PBE	TS	vdW-DF-cx	SCAN+rVV10	uMBD	Exp
Li _{0→1} CoO ₂	R $\bar{3}$ m	3.79	3.33	3.60	4.53	3.96	4.10
Li _{0→1} V ₂ O ₅	Pmna	3.43	2.16	3.08	3.58	3.40	3.60
Li _{0→1} SnS ₂	P $\bar{3}$ m1	1.57	0.25	1.72	1.72	1.72	1.95
Li _{0→1} TiS ₂	P $\bar{3}$ m1	1.86	1.08	1.98	2.09	2.09	2.10
MAE		0.27	1.23	0.34	0.17	0.14	
z-axis lattice parameter, delithiated (Å)							
System	Space group	PBE	TS	vdW-DF-cx	SCAN+rVV10	uMBD	Exp
CoO ₂	R $\bar{3}$ m	16.9	13.8	13.5	12.8	14.7	13.44
V ₂ O ₅	Pmna	11.4	10.1	10.0	9.6	10.1	10.042
SnS ₂	P $\bar{3}$ m1	6.9	6.1	5.8	5.9	6.1	5.88 ^a
TiS ₂	P $\bar{3}$ m1	6.6	5.5	5.6	5.8	5.8	5.695
MAE		1.7	0.2	0.1	0.3	0.4	
z-axis lattice parameter, lithiated (Å)							
System	Space group	PBE	TS	vdW-DF-cx	SCAN+rVV10	uMBD	Exp
LiCoO ₂	R $\bar{3}$ m	14.1	13.1	13.8	13.8	14.2	14.047
LiV ₂ O ₅	Pmna	11.0	10.5	10.5	10.3	10.9	10.664
LiSnS ₂	P $\bar{3}$ m1	6.5	6.2	6.4	6.4	6.3	7.9 ^b
LiTiS ₂	P $\bar{3}$ m1	6.4	5.9	6.3	6.3	6.1	6.188
MAE		0.5	0.8	0.5	0.6	0.5	

Table S3. List of benchmark systems. The list of benchmark systems for the evaluation of the uMBD method in this work as well as the current van der Waals corrected DFT methods.

Category	Systems	Ref
<i>S22 set</i>	22 molecular pairs	<i>S8</i>
<i>X23 set</i>	23 crystals of organic molecules	<i>S9</i>
<i>s-metal set</i>	alkali metals (Li, Na, K, Rb, Cs) alkaline earth metals (Be, Mg, Ca, Sr, Ba) transition metals (Zn and Cd).	<i>S10-S12</i>
<i>ionic-xtal set</i>	LiF, LiCl, LiBr, LiI, NaH, NaF, NaCl, NaBr, NaI, KH, KF, KCl, KBr, KI, RbH, RbF, RbCl, RbBr, RbI, CsH, CsF, CsCl, CsBr, CsI, MgO, CaO, SrO, BaO	<i>S13-S24</i>
<i>mol-ads set</i>	Benzene/Ag(111), CO/Ir(111), CH ₄ /Pt(111), CO/Pt(111), H ₂ O/Pt(111), benzene/Pt(111), C ₂ H ₆ /Pt(111), C ₃ H ₈ /Pt(111), C ₄ H ₁₀ /Pt(111), C ₆ H ₁₀ /Pt(111), benzene/Au(111)	<i>S25</i>
<i>Layered materials</i>	Graphite MoS ₂ <i>h</i> -BN	<i>S26-S31</i> <i>S32</i> <i>S32,S33</i>

Table S4. Benchmark test for various systems. The mean absolute errors (MAEs) and mean absolute percentage errors (MAPEs) of energetics based on PBE and PBE + various van der Waals correction methods and nonlocal van der Waals density functionals in the systems of diverse types of interactions.

MAE (kcal/mol)	<i>S22 set</i>	<i>X23 set</i>	<i>s-metal set</i>	<i>ionic-xtal set</i>	<i>mol-ads set</i>
PBE	2.72	12.1	3.1	3.6	9.7
vdW-corrected DFT methods					
TS	0.31	3.1	35.0	22.7	5.3
TS+SCS	0.33	2.2	12.9	7.2	-
MBD@rsSCS	0.61	1.1	16.4	3.2	4.5
MBD@rsSCS/FI	0.63	1.2	24.2	2.0	5.4
Nonlocal density functionals					
vdW-DF-cx	0.42	2.1	1.6	3.3	11.9
SCAN+rVV10	0.69	2.1	3.5	6.5	6.9
This work					
uMBD	0.54	1.2	3.7	2.9	4.5
MAPE (%)	<i>S22 set</i>	<i>X23 set</i>	<i>s-metal set</i>	<i>ionic-xtal set</i>	<i>mol-ads set</i>
PBE	57.1	61.7	9.9	5.12	59.8
vdW-corrected DFT methods					
TS	8.3	16.6	140.7	35.04	36.4
TS+SCS	7.4	11.9	38.6	9.27	-
MBD@rsSCS	10.4	6.2	48.7	4.63	26.4
MBD@rsSCS/FI	9.6	6.8	65.7	3.13	27.1
Nonlocal density functionals					
vdW-DF-cx	9.2	10.8	3.8	4.05	89.4
SCAN+rVV10	9.3	10.3	8.8	7.57	30.7
This work					
uMBD	8.7	6.8	9.2	3.65	26.6

Table S5. Benchmark test for *s-metal set*. Calculated equilibrium volume (V), cohesive energy (E_{coh}), and bulk modulus (B) of s-block metals using PBE, PBE + van der Waals correction methods and nonlocal van der Waals density functionals. Mean absolute percentage errors (MAPEs) computed with respect to the experimental values in Ref. (S10) and elsewhere are included for comparisons.

V (Å ³ /atom)	PBE	TS	TS +SCS	MBD @rsSCS	MBD @rsSCS/FI	vdW- DF-cx	SCAN +rVV10	uMBD	Exp.
Li	20.3	8.9	15.1	15.7	16.8	20.6	20.6	19.1	20.51
Na	38.0	32.5	28.5	26.8	25.2	38.4	36.1	34.8	37.31
K	73.5	33.5	60.3	70.0	crashed	73.2	72.0	70.3	70.79
Rb	91.0	34.4	74.4	84.0	crashed	89.0	91.1	87.1	86.68
Cs	115.8	34.2	95.2	116.5	crashed	107.4	117.4	110.0	110.12
Be	7.9	7.2	7.6	7.5	7.5	8.1	7.9	7.7	7.82 ^a
Mg	22.8	20.4	21.9	20.9	21.2	22.9	22.5	22.3	22.65 ^a
Ca	42.3	34.6	37.2	37.3	37.0	41.0	42.4	40.9	42.81
Sr	54.6	62.6	47.0	46.6	43.9	52.3	55.6	52.9	55.22
Ba	63.5	63.4	52.8	51.3	48.8	58.3	63.1	61.1	62.31
Zn	15.2	14.0	14.6	14.3	14.4	14.5	13.8	14.7	15.21 ^a
Cd	23.1	21.2	22.2	21.6	21.6	21.2	21.2	22.6	21.44 ^a
MAE	1.8	20.3	7.8	5.3	5.5	1.9	1.8	1.3	
MAPE	2.6	26.1	12.5	10.5	13.6	3.2	2.7	3.1	

E_{coh} (kcal/mol)	PBE	TS	TS +SCS	MBD @rsSCS	MBD @rsSCS/FI	vdW- DF-cx	SCAN +rVV10	uMBD	Exp.
Li	37.4	89.1	60.8	65.5	67.5	38.3	37.7	42.2	38.5
Na	24.9	59.2	43.9	52.4	80.5	26.3	26.4	29.2	26.1
K	20.0	92.3	33.2	34.3	crashed	21.8	21.2	20.3	21.7
Rb	17.6	91.6	29.7	32.0	crashed	19.9	19.0	20.6	19.8 ^b
Cs	16.4	118.3	26.2	26.0	crashed	18.9	17.5	18.9	18.7 ^b
Be	86.0	98.3	93.5	96.8	96.8	84.3	88.9	92.5	79.6 ^a
Mg	34.7	45.9	42.9	48.4	48.1	36.8	41.2	39.9	35.6 ^a
Ca	43.9	58.0	64.5	65.0	66.9	47.3	50.1	48.9	42.9 ^b
Sr	37.1	57.4	58.0	62.7	71.4	41.3	44.1	42.0	40.0 ^b
Ba	43.3	72.2	66.0	75.8	89.4	49.3	49.7	48.1	44.1 ^b
Zn	25.3	35.0	31.7	35.7	35.4	31.6	38.3	31.2	31.8 ^a
Cd	16.9	25.9	24.3	28.5	27.8	25.2	27.7	21.9	27.2 ^a
MAE	3.1	35.0	12.9	16.4	24.2	1.6	3.5	3.7	
MAPE	9.9	140.7	38.6	48.7	65.7	3.8	8.8	9.2	

B (GPa)	PBE	TS	TS +SCS	MBD @rsSCS	MBD @rsSCS/FI	vdW- DF-cx	SCAN +rVV10	uMBD	Exp.
Li	15.2	85.7	25.1	24.9	15.3	13.4	13.4	17.2	13.3
Na	7.8	16.9	14.7	17.0	60.0	6.4	8.0	9.5	7.5

K	3.6	44.1	5.7	4.0	crashed	2.7	4.1	4.4	3.7
Rb	2.6	34.0	4.1	3.7	crashed	2.7	2.9	3.1	2.9
Cs	1.8	63.3	2.7	2.6	crashed	1.6	1.9	1.9	2.1
Be	121.2	144.1	135.7	135.0	137.5	115.1	124.9	130.8	108.1 ^a
Mg	35.7	44.2	39.1	47.4	41.3	36.0	38.2	37.6	38.6 ^a
Ca	17.0	15.7	20.8	21.6	22.0	17.4	18.6	18.1	18.4
Sr	11.6	8.8	16.5	15.6	29.7	11.3	11.2	12.1	12.4
Ba	8.8	9.9	12.3	13.2	26.9	9.6	8.4	9.2	9.3
Zn	73.2	105.4	83.2	91.8	91.8	83.5	104.0	81.4	64.7 ^a
Cd	47.2	61.0	51.2	50.8	57.7	57.9	62.3	53.7	50.7 ^a
MAE	2.8	26.2	6.6	8.0	17.7	3.4	6.0	4.3	
MAPE	8.7	494.1	36.8	37.5	128.2	12.1	12.5	12.4	

^a Ref. (S11)

^b Ref. (S12)

Table S6. Benchmark test for *ionic-xtal* set. Calculated lattice parameter (a) and atomization energy (E_{at}) of ionic crystals using PBE, PBE + various van der Waals correction methods and nonlocal van der Waals density functionals. Mean absolute errors (MAEs) and mean absolute percentage errors (MAPEs) computed with respect to the experimental values for comparisons.

a (Å)	PBE	TS	TS +SCS	TS/HI	MBD @rsSCS	MBD @rsSCS/FI	vdW- DF-cx	SCAN +rVV10	uMBD	Exp.
LiF	4.066	3.671	3.958	4.054	crashed	4.053	4.044	3.961	4.053	4.030 ^a
LiCl	5.147	4.955	5.034	5.169	crashed	5.274	5.093	5.061	5.165	5.140 ^a
LiBr	5.509	5.524	5.354	5.569	5.692	5.602	5.440	5.419	5.569	5.500 ^a
LiI	6.022	5.888	5.809	6.074	6.046	6.031	5.938	5.952	6.028	6.010 ^a
NaH	4.831	5.022	4.666	5.095	crashed	4.758	4.862	4.742	4.800	4.900 ^b
NaF	4.705	4.852	4.601	4.699	crashed	4.691	4.690	4.539	4.695	4.630 ^a
NaCl	5.697	5.362	5.562	5.732	5.754	5.661	5.655	5.537	5.675	5.640 ^a
NaBr	6.038	5.578	5.861	6.074	6.009	5.991	5.983	5.874	6.015	5.980 ^a
NaI	6.533	6.000	6.298	6.558	6.334	6.464	6.454	6.384	6.507	6.470 ^a
KH	5.702	5.202	5.524	5.766	crashed	5.405	5.669	5.614	5.671	5.700 ^b
KF	5.432	5.119	5.326	5.476	crashed	5.411	5.367	5.278	5.350	5.350 ^a
KCl	6.386	5.532	6.296	6.385	6.584	6.300	6.304	6.229	6.333	6.290 ^a
KBr	6.713	5.760	6.608	6.695	6.835	6.609	6.613	6.538	6.662	6.600 ^a
KI	7.188	6.287	7.055	7.095	7.244	7.056	7.064	7.007	7.125	7.070 ^a
RbH	6.058	5.300	5.869	5.247	6.230	crashed	5.979	5.951	6.018	6.040 ^b
RbF	5.755	5.250	5.643	5.255	crashed	crashed	5.661	5.590	5.731	5.650 ^a
RbCl	6.709	5.728	6.604	5.737	6.872	crashed	6.595	6.547	6.660	6.580 ^a
RbBr	7.025	6.038	6.910	6.043	7.126	crashed	6.898	6.849	6.966	6.890 ^a
RbI	7.494	6.724	7.349	6.694	7.510	crashed	7.347	7.317	7.418	7.340 ^a
CsH	6.445	5.422	6.287	6.252	6.615	5.938	6.306	6.312	6.403	6.370 ^b
CsF	6.128	5.426	6.038	5.976	crashed	6.044	6.003	5.959	6.068	6.000 ^c
CsCl	4.211	3.849	4.143	4.110	4.274	4.088	4.086	4.094	4.136	4.110 ^d
CsBr	4.395	3.941	4.324	4.288	4.455	4.260	4.260	4.273	4.326	4.300 ^d
CsI	4.672	4.145	4.590	4.523	4.697	4.519	4.145	4.555	4.598	4.560 ^d
MgO	4.248	4.185	4.226	4.230	4.216	4.198	4.223	4.181	4.227	4.210 ^e
CaO	4.841	4.710	4.786	4.811	crashed	crashed	4.788	4.786	4.831	4.810 ^f
SrO	5.210	5.066	5.151	5.121	crashed	crashed	5.148	5.152	5.199	5.160 ^g
BaO	5.616	5.467	5.556	5.497	crashed	crashed	5.546	5.557	5.609	5.540 ^h
MAE	0.073	0.414	0.067	0.174	0.165	0.075	0.039	0.059	0.047	
MAPE	1.297	7.042	1.222	2.847	2.781	1.359	0.783	1.063	0.856	

E_{at} (kcal/mol)	PBE	TS	TS +SCS	TS/HI	MBD @rsSCS	MBD @rsSCS/FI	vdW- DF-cx	SCAN +rVV10	uMBD	Exp.
LiF	102.5	123.1	114.3	103.1	crashed	103.3	104.8	112.9	103.4	101.5 ⁱ
LiCl	78.5	89.6	89.0	79.8	crashed	80.1	82.4	87.5	79.9	81.9 ⁱ
LiBr	70.3	81.8	80.7	72.0	79.4	72.9	74.8	79.1	72.1	74.9 ⁱ
LiI	61.4	74.6	71.9	64.7	71.9	65.8	66.7	69.2	64.2	63.9 ⁱ
NaH	43.1	61.6	53.6	45.6	crashed	51.7	47.4	47.2	45.3	44.9 ⁱ
NaF	91.0	109.3	101.5	91.9	crashed	92.0	93.2	101.4	92.1	90.6 ⁱ
NaCl	72.3	91.5	82.7	74.3	84.4	74.1	75.9	81.7	73.9	76.2 ⁱ
NaBr	65.1	82.1	75.4	67.3	77.7	67.2	69.3	74.4	66.7	69.3 ⁱ
NaI	57.1	70.9	68.0	60.6	70.5	59.6	62.0	65.6	59.0	60.0 ⁱ
KH	40.8	85.8	48.9	46.3	crashed	49.2	45.7	44.6	42.4	43.5 ⁱ

KF	88.4	133.9	96.9	91.6	crashed	90.6	91.5	98.0	90.5	87.7 ⁱ
KCl	73.3	105.6	81.2	77.1	82.3	76.3	77.1	82.2	75.8	77.2 ⁱ
KBr	66.9	92.8	74.9	70.9	76.8	70.1	71.1	75.8	69.3	71.0 ⁱ
KI	59.7	78.3	68.6	65.1	71.5	63.2	64.6	68.1	62.3	62.6 ⁱ
RbH	38.8	88.4	46.6	84.9	46.3	crashed	44.1	42.8	40.3	41.9 ^{ij}
RbCl	71.9	101.7	79.6	100.3	81.4	crashed	76.0	80.7	74.0	79.7 ^k
RbBr	65.8	88.6	73.6	87.6	76.0	crashed	70.3	74.7	68.1	76.3 ^k
RbI	59.0	75.7	67.5	75.0	71.1	crashed	64.0	67.3	61.6	72.4 ^k
CsH	38.1	99.1	44.5	46.7	42.7	46.1	44.1	42.2	39.6	41.1 ^{il}
CsF	84.9	143.5	91.7	92.4	crashed	89.0	89.0	94.7	87.3	84.9 ⁱ
CsCl	70.7	111.6	78.5	78.3	78.3	76.0	76.7	81.2	74.9	76.6 ⁱ
MgO	119.4	127.8	124.9	121.4	121.3	127.5	124.5	132.4	123.2	118.3 ⁱ
CaO	129.4	142.0	142.9	132.0	crashed	crashed	135.6	141.7	132.6	126.2 ⁱ
SrO	120.7	133.8	134.4	133.0	crashed	crashed	127.1	133.2	123.7	119.6 ⁱ
BaO	117.8	133.3	131.4	132.2	crashed	crashed	124.9	129.3	120.7	116.3 ⁱ
MAE	3.6	22.7	7.2	6.2	13.3	8.4	13.6	27.3	12.3	
MAPE	5.1	35.0	9.3	9.5	4.6	3.1	4.0	7.6	3.7	

^a Ref. (S13)

^b Ref. (S14)

^c Ref. (S15)

^d Ref. (S16)

^e Ref. (S17)

^f Ref. (S18)

^g Ref. (S19)

^h Ref. (S20)

ⁱ Ref. (S21)

^j Ref. (S22)

^k Ref. (S23)

^l Ref. (S24)

Table S7. Benchmark test for *mol-ads* set. The adsorption energy of molecule on transition metal surface based on PBE and PBE + various van der Waals correction methods compared with the experimental data from Ref. (S25).

E_{ads} (kcal/mol)	PBE	TS	TS/HI	MBD @rsSCS	MBD @rsSCS/FI	vdW- DF-cx	SCAN +rVV10	uMBD	Exp.
benzene/Ag(111)	-1.4	-18.2	-18.1	-12.0	-14.0	18.1	-15.1	-11.5	-14.6
CO/Ir(111)	-45.0	-49.2	-49.0	-49.7	-50.2	-42.9	-52.5	-48.9	-39.2
CH ₄ /Pt(111)	-3.1	-8.0	-7.7	-6.1	-6.4	-13.8	-6.6	-6.0	-3.3
CO/Pt(111)	-37.8	-42.6	-42.9	-42.8	-44.0	-36.7	-49.7	-42.4	-29.6
H ₂ O/Pt(111)	-4.6	-9.3	-9.3	-8.4	-9.2	-12.9	-11.8	-8.4	-13.1
benzene/Pt(111)	-21.4	-47.4	-49.6	-44.9	-51.2	-24.1	-60.6	-44.5	-38.7
C ₂ H ₆ /Pt(111)	-0.5	-8.1	-8.2	-5.8	-6.2	-9.7	-6.3	-5.6	-6.5
C ₃ H ₈ /Pt(111)	-1.3	-12.7	-12.7	-9.1	-9.8	-9.0	-9.4	-8.8	-9.3
C ₄ H ₁₀ /Pt(111)	-0.8	-14.7	-14.7	-10.2	-11.3	-6.0	-10.9	-9.9	-11.5
C ₆ H ₁₀ /Pt(111)	-15.4	-35.7	-36.4	-32.2	-39.1	-11.7	-41.1	-31.9	-29.4
benzene/Au(111)	-1.8	-17.0	-16.6	-11.9	-13.7	18.3	-14.1	-12.0	-16.7
MAE	9.7	5.3	5.6	4.5	5.4	11.9	6.9	4.5	
MAPE	59.8	36.4	36.2	26.4	27.1	89.4	30.7	26.6	

Table S8. Benchmark test for layered materials. The equilibrium distance and interlayer binding energy of AB-stacked graphite, hexagonal molybdenum disulfide (2H-MoS₂), and AA'-stacked hexagonal boron nitride (*h*-BN) based on PBE, PBE + van der Waals correction methods and nonlocal van der Waals density functionals in comparison with high-level theoretical methods and experiments.

Graphite (AB)	Equilibrium distance Å	Binding energy kcal/mol
PBE	4.42	0.02
TS	3.36	1.84
MBD@rsSCS	3.38	1.12
MBD@rsSCS/FI	3.38	1.19
uMBD (this work)	3.32	1.22
ACFDT-RPA ^a	3.34	1.11
QMC ^b	3.426	1.29
vdW-DF-cx ^c	3.29	1.49
SCAN+rVV10 ^d	3.32	1.08
Experiment	3.336 ^e	0.99 ^f , 0.81 ^g , 1.20 ^h

2H-MoS ₂	<i>c</i> -axis lattice parameter Å	Binding energy kcal/mol
PBE	14.9	0.02
TS	12.1	1.92
MBD@rsSCS	12.3	0.88
MBD@rsSCS/FI	12.2	1.11
uMBD (this work)	12.5	0.81
ACFDT-RPA		0.68 ⁱ
vdW-DF-cx ^c	12.3	1.19
SCAN+rVV10 ^d	12.5	1.04
Experiment ⁱ	12.290 – 12.530	

<i>h</i> -BN (AA')	Equilibrium distance Å	Binding energy kcal/mol
PBE	4.29	0.04
TS	3.32	2.01
MBD@rsSCS	3.33	1.23
MBD@rsSCS/FI	3.31	1.18

uMBD (this work)	3.25	1.12
ACFDT-RPA ⁱ	3.30	0.90
vdW-DF-cx ^c	3.25	1.52
SCAN+rVV10 ^d	3.30	1.22
Experiment ^j	3.301	

^a Ref. (S26)

^b Ref. (S27)

^c Ref. (S1)

^d Ref. (S2)

^e Ref. (S28)

^f Ref. (S29)

^g Ref. (S30)

^h Ref. (S31)

ⁱ Ref. (S32)

^j Ref. (S33)

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