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Author(s): Björkman, T. & Gulans, A. & Krasheninnikov, A. V. & Nieminen, Risto M.

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van der Waals Bonding in Layered Compounds from Advanced Density-Functional First-Principles Calculations

T. Björkman,¹ A. Gulans,¹ A. V. Krasheninnikov,^{1,2} and R. M. Nieminen¹

¹*COMP - Aalto University School of Science, P.O. Box 11100, 00076 Aalto, Finland*

²*Department of Physics, University of Helsinki, P.O. Box 43 00014 Helsinki, Finland*

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Although the precise microscopic knowledge of van der Waals interactions is crucial for understanding bonding in weakly bonded layered compounds, very little quantitative information on the strength of interlayer interaction in these materials is available, either from experiments or simulations. Here, using many-body perturbation and advanced density-functional theory techniques, we calculate the interlayer binding and exfoliation energies for a large number of layered compounds and show that, independent of the electronic structure of the material, the energies for most systems are around 20 meV/Å². This universality explains the successful exfoliation of a wide class of layered materials to produce two-dimensional systems, and furthers our understanding the properties of layered compounds in general.

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Recent progress in the mechanical [1,2] and chemical [3,4] exfoliation of weakly bonded layered inorganic compounds, such as BN, MoS₂, WSe₂, Bi₂Se₃, Bi₂Te₃, raises prospects for manufacturing two-dimensional materials which can be used in a plethora of applications [5]. The optimization of the exfoliation process should be helped by a precise knowledge of the interlayer bonding in the parent layered compounds, data which are currently unavailable. This lack of data is also hampers the studies of the layered compounds themselves, which can be topological insulators [6], thermoelectrics [7], charge-density-wave materials [8], and superconductors [9].

Two closely related quantities, the binding energy, E_B , between the layers and the energy required to remove an individual layer, the exfoliation energy, E_{XF} , are of crucial importance for optimizing the process to produce a two-dimensional structure, as well as for understanding the interlayer bonding in the three-dimensional parent materials. Unfortunately, essentially no information on the interlayer bonding is available from experiments, with the only exception being graphite [10–12]. Moreover, the standard first-principles computational approaches based on density-functional theory (DFT) with widely used local and semilocal exchange and correlation functionals are of little help, since these functionals fail to account for the nonlocal van der Waals (vdW) interactions between the layers, as has been demonstrated for graphite [13,14].

Recently, however, several methodologies that are able to handle vdW interactions have become available for calculations. In this Letter, we apply two of these, the nonlocal correlation functional method (NLCF) of Refs. [15–17], and the adiabatic-connection fluctuation-dissipation theorem within the random-phase approximation (RPA) [18–20] to study the interlayer binding of layered compounds. The NLCF approach is free from material specific parameters and has been shown to be in

good agreement with experimental data for various systems [15,16]. RPA is expected to be highly accurate in the limit of long wavelength fluctuations involved in the vdW interaction between distant objects [21] and has served as the basis for analytic vdW theory for a long time [22], but is less accurate for short-range interactions involved in the covalent bonding in solids [23,24]. This has been addressed in a number of recent works aiming to improve the properties of the RPA by introducing further terms in the many-body interaction [24,25] and by the introduction of approximations to the exchange-correlation kernel [26]. However, these extensions come at a formidable computational cost and the short-range deficiency mostly affects the total correlation energy and is less serious when comparing energy differences [23]. The RPA approach has been demonstrated to produce accurate results for small molecules [27], atomization energies in solids [20,28], surface and adsorption energies [29], and the binding of graphite [30]. In an attempt to get a bird's-eye view of the typical behavior of the interlayer bonding in weakly bonded layered materials, we perform high-throughput calculations for a large set of compounds, identified by data mining techniques to be likely candidates for layered structures with predominantly vdW types of interactions between the layers. Unfortunately, the RPA is currently prohibitively expensive from the computational point of view to be used as the standard method of choice, and is applied here as a reference for a smaller set of compounds.

A set of layered compounds were selected by searching the Inorganic Crystal Structure Database [31] and applying geometric criteria to identify vdW-bonded layered structures. The criteria were based on the packing ratio of the crystal, identification of gaps in the structure along the crystallographic c axis, and verification that the interlayer bonds were elongated beyond what is expected for covalent bonds by comparison with the sum of the covalent

radii. The filtering procedure is described in detail in the Supplemental Material [32]. The benefit of this procedure is that it will generate a selection unbiased by our own expectations and previous knowledge, thus providing a more diverse set. From the generated list of compounds, we selected a subset of tetragonal and hexagonal or trigonal systems and further enlarged the list by making sure that all reported layered compounds of transition metal dichalcogenides (MX_2 , with M being a transition metal and X being either S, Se, or Te) were on the list. After the removal of some of the most computationally demanding systems, we arrive at a mixed set of 86 compounds—metals, semimetals, insulators, and magnetic compounds. Apart from the MX_2 compounds, the list thus obtained contains many important materials, such as graphite, BN, and the topological insulators Bi_2Se_3 and Bi_2Te_3 . All calculations were performed using the projector augmented wave method as implemented in the electronic structure package VASP [33,34]. We used an in-house NLCF implementation [35] and the standard VASP implementation of RPA [20]. Crystal geometries were automatically generated from database searches using the program CIF2CELL [36].

The procedure for calculating E_B is illustrated schematically in Figs. 1(a) and 1(b). In order to get accurate estimates of E_B , a general assessment of the different DFT-based approaches was necessary. The list of investigated methods included the local density approximation (LDA), the semiempirical method by Grimme [37,38]

[dispersion-corrected Perdew–Burke–Ernzerhof functional (PBE-D)] as well as the NLCF methods by Dion *et al.* [15] (vdW-DF1), Lee *et al.* [16] (vdW-DF2), and Vydrov and van Voorhis [17] (VV10). We compared the calculated interlayer binding energies to the more sophisticated many-body treatment of RPA for a subset of layered compounds, and studied how well the different DFT-based approaches reproduce the reported vdW bond lengths, the only experimental data pertaining to the vdW interaction that is available for all compounds.

The conclusion is that all NLCF methods reproduce the RPA trends of E_B sufficiently well to be useful for predicting interlayer binding energies, whereas two other popular choices for treating vdW interactions, LDA and PBE-D, do not [39]. In fact, any of the NLCF type of functionals can be rescaled by its average deviation from the calculated RPA values to yield an estimate of the RPA energy, limited primarily by the inaccuracies in equilibrium bond lengths. In particular, we find that the VV10 [17] functional is highly successful, both for producing accurate geometries and following the E_B trends of RPA very closely, so that an accurate estimate of the RPA binding energy can be obtained by simply rescaling the VV10 results by a factor of 0.66, and we will henceforth refer to this as the *NLCF estimate* of the binding energy. It should be noted that this estimate is purely based on the empirical observation of the trends for the 28 compounds investigated by RPA. This is illustrated in Fig. 1, where a representative set of the calculations are shown, first as a demonstration of the

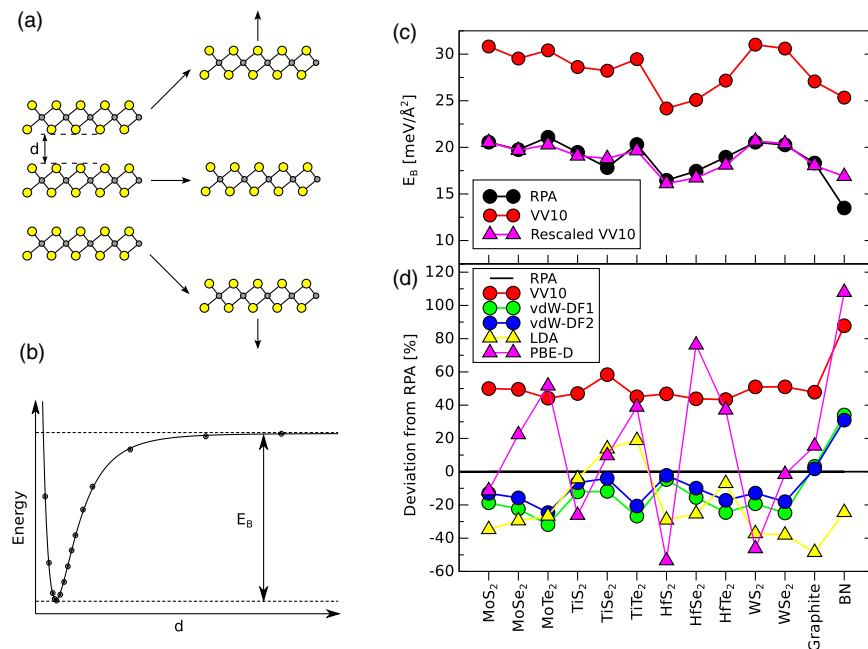


FIG. 1 (color online). (a) Procedure for calculating the interlayer binding energy by increasing the interlayer distance, d . (b) Schematic illustration of a binding energy curve. (c) A set of interlayer binding energies calculated using the RPA and the VV10 functional, demonstrating how a rescaling of the VV10 values can be used to match the more computationally demanding RPA values. (d) Comparison chart for a number of different functionals widely used for treating vdW interactions relative to the RPA results.

effect of the rescaling in panel (c), and then by a comparison of a set of different functionals in terms of their relative deviations from RPA in panel (d). We also point out that RPA is superior to all other methods at reproducing the experimental vdW interplanar bond lengths, with a maximal deviation of 4%, thus further demonstrating the high accuracy of RPA for vdW bonding in layered compounds. The full data set used for the functional comparison is available in the Supplemental Material, Secs. II and IV [32].

The smaller set of E_B calculated using RPA and the full set estimated by the rescaling of the VV10 data, are shown in Fig. 2. The peak of the distribution is around 13–21 meV/Å² (taken as 1 standard deviation around the average of the distribution), with a tail that is slightly more significant toward lower than toward higher binding energies. This region contains, among other compounds, graphite and BN, and also most of the MX_2 compounds. There are outliers in the distribution at slightly higher binding energies, consisting primarily of the Co family ditellurides and NiTe₂ and PdTe₂. These compounds have significant binding energies (15–25 meV/Å²) even when calculated using a regular generalized-gradient approximation (GGA) functional, which normally produces little or no binding for vdW-bonded systems. This indicates that, although there are contributions also from covalent interactions captured by the GGA type functional, in a few cases, the size of the vdW component of the binding remains the same. We have not been able to find correlations of E_B to any other quantity in the present set of compounds. The quantities scanned for such correlations were the interlayer distances, intralayer thicknesses, and band gap or metallicity, as well as properties of the constituent atoms such as the atomic weights and polarizabilities. Nor can we find any reason such as simple band filling arguments that

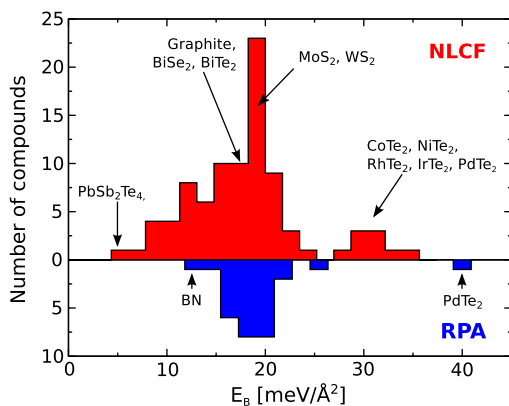


FIG. 2 (color online). Distribution of binding energies estimated from a NLCF (VV10), and distribution of the binding energies calculated by RPA, in blue. The vast majority of the compounds fall in the interval ~ 13 – 21 meV/Å². We also mark in which histogram bin some particular compounds are. The outliers on the high binding energy side around 30 meV/Å² are mostly a set of tellurides where weak covalent bonds contribute as well.

would give any correlation to the binding energies. We conclude that the strength of the vdW bonds in layered solids is a universal quantity. Such a universality is in line with observations by Coleman *et al.* [3,4], based on the experimental data on chemical exfoliation of a large set of MX_2 and Bi₂Te₃ compounds. Detailed information on the binding energies for specific compounds is tabulated in the Supplemental Material, Sec. IV [32].

The statement of universality of the vdW component of the binding energy of layered compounds raises the question whether our initial selection criteria might have been biased in such a way that we only find compounds with a vdW component of the binding energy in this range. Within a given selection it is of course never possible to validate the selection itself, but we nevertheless gain confidence by the lack of correlation to any conspicuous quantity within our selection. It is hard to see how one could arrive at some group of compounds with different binding properties in such a way that it does not constitute a variation of some the properties to which we have found no correlation within our data set.

In view of the known qualitative differences between metals and semiconductors for large separations [40], the observed universality seems counterintuitive, but can be understood through simple arguments. The binding energy is determined by the balance of the repulsive and attractive parts of the interaction near the equilibrium geometry, and these quantities depend on the electron density profile. The repulsive part stems from the exchange interactions and can be estimated well based on the electronic density alone [41]. Similar considerations apply to the attractive vdW interactions, described, e.g., by Zaremba and Kohn [42], who derived a form for the high-frequency–long-wavelength limit of the density response of a surface in terms of the density profile, and were also among the arguments leading up to the original formulation of the NLCF method [43]. As the density profiles of different vacuum interfaces show similar exponential decays, we can understand why the vdW component of the binding is constant and larger variations come from covalent bonding.

Taking into account the recent interest in layered MX_2 systems [3,4] we present in Fig. 3 E_B for all layered forms of MX_2 compounds, which are found in the early and late transition metal d series. We have also filled out some gaps among the experimentally reported structures by calculations for hypothetical layered structures of CrTe₂, TcSe₂, TcTe₂, ReTe₂, NiS₂, and NiSe₂. The crystallographic parameters for these compounds are reported in the Supplemental Material, Sec. III [32]. Our findings are shown in Fig. 3, illustrating the variation of E_B as we move across the transition metal series, and by the respective chalcogen species. Most energies fall in the region $E_B = 15$ – 20 meV/Å² and, as a rule, the factor that most strongly determines the binding energy appears to be the

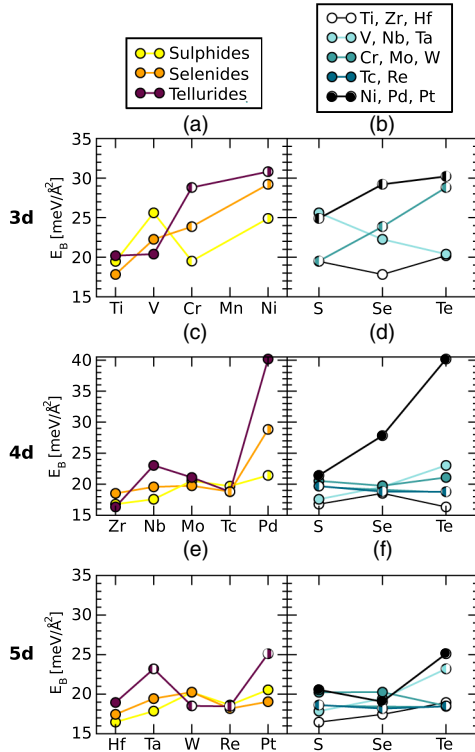


FIG. 3 (color online). Interlayer binding energies of the transition metal dichalcogenides. Panels (a), (c), and (e) show the variation of the binding energy with respect to the transition metal species and panels (b), (d), and (f) show the variation of the binding energy with respect to the chalcogen species. The rows stand for the 3d, 4d, and 5d transition metal series, respectively. Solid circles are the results of the RPA calculations and a striped pattern indicates a value obtained from the NLCF (VV10) calculations. In panels (c) and (d), PdTe₂ has a significantly higher binding energy than the other compounds.

transition metal species, while the dependency on the chalcogen species is weaker. Exceptions to these rules are found among the Cr compounds and the Co and Ni family tellurides, which, as previously discussed, have large covalent and electrostatic contributions to the binding energies. Inasmuch as the atomic polarizabilities vary smoothly as function of the transition metal or chalcogen species [44], the lack of persistent trends in Fig. 3 is important. This demonstrates the importance of a correct description of the electronic states, incorporating collective effects such as the band formation, to capture trends in the binding energies.

The interlayer binding energy is closely related to the exfoliation energy, E_{XF} , the cost of removing a single layer from the surface of the bulk compound. It is expected that $E_{\text{XF}} \approx E_B \approx 2E_{\text{surf}}$, where E_{surf} is the surface energy, and this point is further explained in Sec. IV of the Supplemental Material [32]. We simulated exfoliation for a series of multilayer systems by peeling off the top layer, as shown in the inset of Fig. 4. The figure demonstrates, for the cases of graphene, BN and MoS₂, how peeling off a

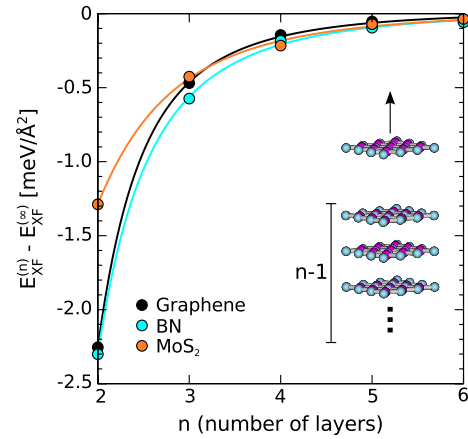


FIG. 4 (color online). Energy required for exfoliation of a single layer from a multilayer structure as a function of the number of layers n as shown schematically in the inset figure. The curves have been fitted to the calculated points as a guide for the eye and the zero of energy has been set to $E_{\text{XF}}^{(\infty)}$; the asymptote of the respective curve as n is taken to infinity. The energy is estimated from NLCF (VV10) calculations.

single layer costs increasingly large amounts of energy as the number of underlying layers increases. This behavior originates from the interaction of the topmost layer with not only its nearest neighbor, but also other layers. However, the difference between E_B and E_{XF} is small, no more than 4%, primarily due to surface relaxation effects, as our calculations for graphene, BN, and all hexagonal, nonmagnetic MX_2 compounds indicate. Thus, the exfoliation energy can be assumed to be equal to the interlayer binding energy in all layered materials, so that our accurate theoretical results for interlayer binding energies are not only important for understanding the properties of bulk layered compounds and inorganic multiwalled nanotubes [45], but should also be useful in the optimization of the exfoliation process.

In conclusion, using advanced calculation techniques, we have shown that the interlayer binding energies of weakly bonded layered compounds are found in a small energy interval of 13–21 meV/Å². These energies fall very close to the exfoliation energies of the compounds, and are of high importance for the understanding of weakly bonded layered solids and their exfoliation into single layers.

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