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The exfoliation energy of black phosphorus revisited: a coupled cluster benchmark

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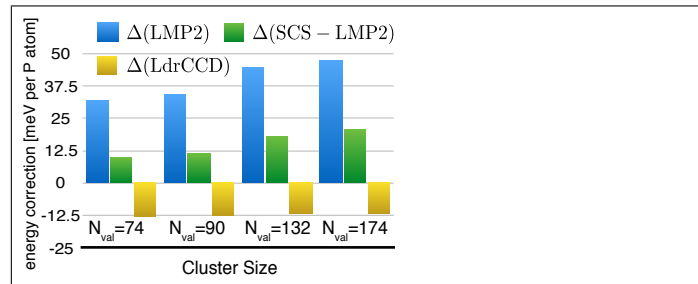
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Abstract

Black phosphorus consists of phosphorene sheets, stacked by van der Waals dispersion. In a recent study based on periodic local second-order Møller-Plesset perturbation theory (LMP2) with higher-order corrections evaluated on finite clusters, we obtained a value of -151 meV/atom for the exfoliation energy. This is almost twice as large as another recent theoretical result (around 80 meV/atom) obtained with Quantum Monte Carlo (QMC). Here, we revisit this system on the basis of the recently implemented, periodically embedded ring-coupled-cluster (rCCD) model instead of LMP2. Higher-order Coupled Cluster corrections on top of rCCD are obtained from finite clusters by utilizing our new “unit-cell-in-cluster” scheme. **Our new value of -92 meV/atom is noticeably lower than that based on LMP2 and in reasonably close agreement with the QMC results. However, in contrast to QMC, no strong effect from the second-neighbor and farther layers in black-P are observed in our calculations.**

Graphical TOC Entry



Black phosphorus, van der Waals interactions in solids, quantum chemical methods

Phosphorus exists in several forms (allotropes); below 550 °C at atmospheric pressure, black phosphorus (black-P) is the thermodynamically most stable allotrope. It has a layered structure consisting of covalently bound sheets (phosphorene layers), which in turn stack up to a crystal by virtue of van der Waals dispersion. GW and Bethe-Salpeter (BSE) equation calculations,^{1,2} as well as experimental measurements³ exhibit a relatively strong dependence of the band gap as a function of the number of phosphorene layers, ranging from around 2 eV for a single sheet to less than 0.5 eV for bulk black-P. Since the discovery of graphene, triggered by its isolation from graphite by mechanical exfoliation,⁴ there is great interest in two-dimensional (2D) materials. Many other 2D materials have been fabricated in the meantime by exfoliation techniques, among them phosphorene.^{5,6} Phosphorene, a hot topic in current research, is a very promising candidate for applications in electronics, optoelectronics, photovoltaics, and spintronics.⁷⁻⁹ A comprehensive recent review can be found in Ref. 10. Since its fabrication process, as just mentioned, is based on exfoliation techniques, the exfoliation energy of black-P is an important quantity. To our knowledge, there is presently no experimental measurement available, hence the only source of information are quantum chemical calculations.^{7,11-17}

In a recent study¹⁷ we investigated black-P, and in particular its exfoliation energy on the basis of periodic local second-order Møller-Plesset perturbation theory (LMP2).¹⁸⁻²¹ LMP2 does not catch van der Waals dispersion. However for strongly polarizable systems LMP2 is known to notoriously overestimate their strength. This also applies to the case of black-P with its small band gap (*vide supra*). Hence, in order to amend this deficiency of the method we employed spin-component-scaled (SCS)-LMP2²² instead of LMP2, which is often considered an inexpensive remedy for the MP2's overbinding. Furthermore, we calculated higher-order corrections relative to SCS-LMP2 for the finite cluster $P_4H_6-P_{16}H_{10}$, which was chosen to mimic the periodic black-P bilayer (the P_4H_6 subunit of the dimer, apart from the saturating H-atoms, just corresponds to the unit cell of black-P). These higher-order corrections take care of basis set, core correlation, and method error.

Based on the periodic SCS-LMP2 calculations and these corrections we obtained a value of $E_{\text{exf}} = -151$ meV/atom for the exfoliation energy.¹⁷ This is substantially larger than another very recently reported value of $E_{\text{exf}} = -80$ meV/atom, as calculated by Shulenburg *et al* by employing fixed node Diffusion Monte Carlo (DMC).¹⁶ Also the interaction energy between two phosphorene layers (an isolated bilayer in AB stacking as in the crystal), referred to in the following as "interaction energy", deviates by more than a factor of two, *i.e.*, -70 vs -30 meV/atom.

In order to rationalize this substantial deviation in the ab initio predictions we revisit the black-P bilayer, using a more advanced quantum chemical technology. Firstly, the level of the periodic treatment is increased from SCS-LMP2 to the newly implemented fragment-based local direct ring-CCD (LdrCCD),²³ embedded in the periodic HF mean field. The LdrCCD method²³⁻²⁵ is related to the second-order screened exchange (SOSEX) variant of the random phase approximation,^{26,27} but in addition to that contains exchange diagrams preserving the antisymmetry of the doubles amplitudes with respect to swapping of the spin-orbital indices of a pair. Importantly, LdrCCD, in contrast to LMP2 or SCS-LMP2, includes the Coulomb-ring diagrams up to all orders, which is commonly referred to as Coulomb screening.²⁸⁻³¹

Secondly, we progressively expanded the finite cluster mimicking the bilayer to reach convergence in the higher-order coupled-cluster corrections. In the previous work,¹⁷ the cluster used for evaluating such corrections was relatively small: $\text{P}_4\text{H}_6\text{-P}_{16}\text{H}_{10}$. The cluster size was actually not restricted by the computational cost of the calculations involved, but rather by the necessity to match the interaction energy obtained for the cluster to that of the periodic system: the P_4H_6 subunit of the $\text{P}_4\text{H}_6\text{-P}_{16}\text{H}_{10}$ dimer just corresponds to the unit cell of the black-P crystal. This restriction is lifted in the present work by our new "unit-cell-in-cluster" scheme, which is only applicable in the framework of a local formalism: a subset of localized occupied orbitals (LMOs) is specified; number and mutual orientation of these LMOs must match those of the Wannier functions in the unit cell of the parental periodic system. Furthermore, in order to minimize the influence of artificial surface effects

the LMOs should be localized *in the center* of the finite cluster. The specified subset of LMOs constitutes the “unit cell”. The equation for the correlation energy for the cluster is then reformulated to be consistent with the periodic correlation energy per cell, to which it also converges numerically with increasing size of the cluster. For a detailed description of this approach we refer to the SI.

Four clusters of increasing size were considered in the present study, *i.e.*, $P_{10}H_8$ – $P_{16}H_{10}$, $P_{16}H_{10}$ – $P_{16}H_{10}$, $P_{16}H_{10}$ – $P_{32}H_{14}$, and $P_{32}H_{14}$ – $P_{32}H_{14}$. Plots of these clusters along with the related cluster “unit cells” are provided below and in the SI.

Fig. 1 presents the interlayer interaction energies obtained within the periodic, the embedded-fragment, and the above mentioned “unit-cell-in-cluster” finite cluster models of the black-P bilayer at different levels of theory ranging from LMP2 up to LCCSD(T). In order to mutually relate the embedded-fragment and finite cluster models, the energies are given as functions of the number of correlated orbitals in the fragment or cluster, which serves here as a measure of their size.

Firstly, the LMP2, SCS-LMP2 and LdrCCD interaction energies reveal that for black-P the non-embedded finite-cluster model nevertheless provides a good description. Indeed, the finite-cluster results at the augmented-triple-zeta basis set level (see SI for the exact basis set specifications) are very close to those of the fragment approach, which is embedded in the correct periodic HF solution. The embedded fragment LMP2 and SCS-LMP2 energies, in turn, converge smoothly to the fully periodic result.

Having established the reliability of our models, we are in the position to discuss the underlying physics of the interaction in black-P. Fig. 1 clearly demonstrates that the convergence of the interaction energy with the cluster or fragment size exhibits two different patterns depending on the method. On the one hand, the LMP2 and SCS-LMP2 methods converge quite slowly. On the other hand, all the coupled cluster models of the present work, ranging from LdrCCD up to the LCCSD(T) exhibit a different convergence pattern: the convergence rate of the interaction energies of these methods, regardless of basis set level,

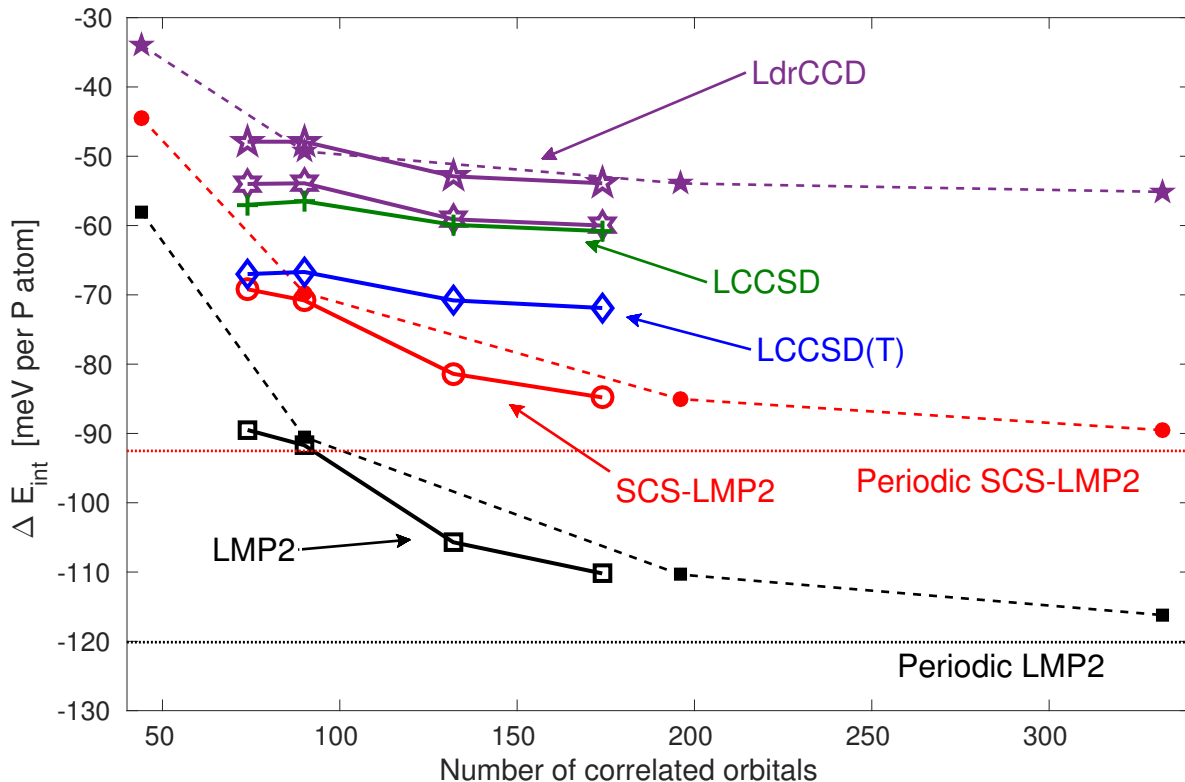


Figure 1: The correlation contributions to the interlayer interaction energies ΔE_{int} (see SI for its exact definition) for the black-P bilayer from the periodic (dotted lines), embedded-fragment (filled symbols) and finite-cluster (open symbols) calculations. ΔE_{int} was computed using LMP2 (squares), SCS-LMP2 (circles), LdrCCD (five and six pointed asterisks), LCCSD (crosses), and LCCSD(T) (diamonds), respectively. The LCCSD and LCCSD(T) calculations were performed within the LCCSD|LCCD[S] r^{-6} and LCCSD(T0)|LCCD[S] r^{-6} approximations.^{24,32} The geometry of the bilayer was taken from Ref.¹⁷, which is very close to the experimental bulk geometry.^{33,34} Periodic and embedded-fragment calculations employed the periodic AVTZ basis. The exact specifications of the geometry, basis sets, and basis set extrapolations are provided in the SI. The presented finite-cluster results correspond to either the aug-cc-pVTZ basis³⁵ (LMP2, SCS-LMP2, and LdrCCD: five pointed asterisk) or to the basis set extrapolation (LdrCCD: six pointed asterisk, LCCSD and LCCSD(T)). The virtual space in these calculations was restricted to core domains.

is much faster than that of LMP2 or SCS-LMP2, and, even more importantly, virtually identical among each other. This implies, that *the differences* between the interaction energies of the various coupled cluster models converge even faster than their individual interaction energies themselves.

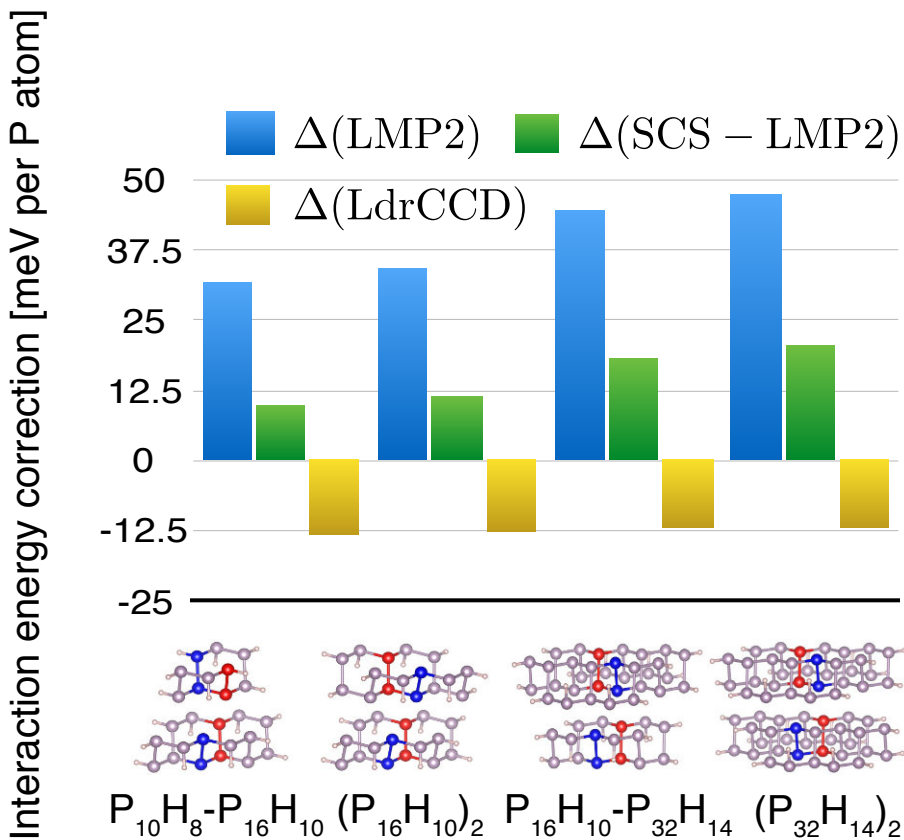


Figure 2: The differences between the LCCSD(T) and the LMP2, SCS-LMP2, or LdrCCD interlayer interaction energies (denoted, respectively, as $\Delta(\text{LMP2})$, $\Delta(\text{SCS-LMP2})$, and $\Delta(\text{LdrCCD})$) for the four different finite clusters. The four clusters are depicted together with their corresponding cluster “unit cells” (atoms colored in blue and red; see SI for details about the meaning of these two colors). The results correspond to the basis set extrapolated interaction energies based on core domains. For LCCSD(T) the LCCSD(T0)|LCCD[S] r^{-6} model^{24,32} was used.

As is evident from Fig. 2, this is indeed the case. Even though the method error of the LdrCCD model $\Delta(\text{LdrCCD})$, *i.e.*, the difference between the LCCSD(T) and LdrCCD interaction energies, is quite noticeable, it is virtually independent of cluster size: it changes

just from -13.0 to -11.9 meV per P atom between smallest and largest cluster. The picture is completely different for SCS-LMP2. For small clusters, $\Delta(\text{SCS-LMP2})$ measuring the deviation of the SCS-LMP2 interaction energy relative to LCCSD(T), is rather small. This fact was used in Ref. 17 as an argument supporting the adequacy of the SCS-LMP2 model. However, with growth of the cluster it increases from $+9.6$ to $+20.6$ meV per P atom, and there is no indication that $\Delta(\text{SCS-LMP2})$ has already converged. On the contrary, given the distinct convergence rates of the interaction energies within these two methods, the convergence of the corresponding energy difference would occur not earlier than the convergence of the individual LCCSD(T) and SCS-LMP2 energies themselves, rendering the correction scheme useless.

The fully periodic LdrCCD result would be an excellent starting point for evaluating a high precision interaction energy, since the higher-order method correction is very insensitive w.r. to the cluster size (as just discussed). Furthermore, it is also quite insensitive w.r. to basis set quality (at least if better than double-zeta) and local approximations, *e.g.*, domain extensions (see the SI for details). Presently, we do not yet have a fully periodic LdrCCD implementation available. Instead we adopt the embedded-fragment results, which for the largest fragment appear to be practically converged, even for the SCS-LMP2 treatment.

Regarding the nature of the interaction between individual layers of black-P, one may anticipate a rather efficient screening of Coulomb interactions, given the narrow band gap of the system.³⁶ This effectively reduces the range of the dispersive interaction between individual phosphorene layers, as is evident from our results. Both LMP2 and SCS-LMP2 capture only unscreened dispersion as they lack the higher-order diagrams required to describe screened interactions. LdrCCD, on the other hand, does include a certain class of such diagrams, *i.e.*, the ring Coulomb diagrams summed to all orders. Apparently, this subset of diagrams is sufficient to describe the van der Waals interactions in black-P at least qualitatively correctly, since the much more sophisticated LCCSD(T) exhibits the same qualitative picture and improves LdrCCD only quantitatively.

The final converged estimate for the interlayer interaction energy of the black-P bilayer, as computed by our new quantum chemical scheme, amounts to -47 meV per P atom. This value is the sum of the following individual contributions: (i) Periodic HF (+40 meV per atom), (ii) embedded-fragment LdrCCD in AVTZ basis (-63 meV per atom), (iii) the correction of the LdrCCD/AVTZ basis set error (-5 meV per atom), (iv) the correction of the LdrCCD method error (-16 meV per atom), and (v) the correlated core contribution (-2 meV per atom). For details on how these individual components were evaluated we refer to the SI, in particular to Table S6.

In order to calculate the exfoliation energy E_{exf} we have to multiply the interaction energy by a factor of two and to add the effect of second-nearest and father layers. In order to assess the latter we performed additional calculations employing, on the one hand, periodic models (bilayer versus 3D crystal) at the HF and SCS-LMP2 levels, and on the other hand black-P-type clusters (dimer vs trimer) at the LdrCCD, LCCSD and LCCSD(T) levels. For a detailed specification of the computational models, collection of the results and supporting discussion we again refer to the SI. It turns out that none of the employed schemes apart from the periodic SCS-LMP2 exhibits a strong effect: the increase or decrease in the exfoliation energy due to the third layer never exceeds one meV (HF: +1.4 meV per P atom, LCCSD(T): -0.2 meV per P atom), *i.e.*, twice the value in Table S7). The periodic SCS-LMP2 results indeed feature an excess in the interaction energy on going from the bilayer to the 3D crystal (about -10 meV per P atom). However, as the results of this work demonstrate, SCS-LMP2 grossly overestimate due to the lack of Coulomb screening. Hence, we rather use the LCCSD(T) finite cluster value plus periodic Hartree Fock. This yields a value for the exfoliation energy of $E_{\text{exf}} = -92$ meV per P atom. This new value is very close to the DMC exfoliation energy of -80 meV per P atom (to which at least about -4 meV per P atom should be added due to core correlation).

According to Ref. 16 the -80 meV per P atom value for the DMC exfoliation energy can actually be dissected into twice the interaction energy of the bilayer (-30 meV per P atom)

plus long-range effects from other layers (-20 meV per P atom). The latter component is much larger than anyone of our estimates, including that of periodic SCS-LMP2. The latter actually includes dispersion-induced charge redistribution,³⁷ which was suggested in Ref. 16 to be the main mechanism of this effect. Yet the SCS-LMP2 long range contribution is only half as large as that of DMC, even though it should *overestimate* long range dispersion due to lack of Coulomb screening.

To conclude, we have revisited black phosphorus, applying a novel and much more elaborate quantum chemical treatment compared to our previous study.¹⁷ Firstly, the periodic treatment was increased to LdrCCD, which unlike LMP2 or SCS-LMP2, captures screened rather than only bare dispersion. Secondly, the finite cluster LCCSD(T) correction, now on top of LdrCCD rather than SCS-LMP2, was converged w.r. to cluster size. Our final result can be considered as a very accurate (close to CCSD(T)/basis-set-limit level) quantum chemical benchmark. This study revealed a significantly weaker binding in this system than that predicted by us previously in Ref. 17 (-47 *vs* -70 meV per P atom for the bilayer interaction energy; -92 *vs* -151 meV per P atom for the exfoliation energy). Our new exfoliation energy agrees very well with that of the DMC study of Ref. 16. Yet our bilayer interaction energy is about 15 meV per P atom more binding than the DMC result. In contrast to DMC, we have not observed any strong influence of the third and farther layers on the interaction energy.

This work can also be seen as a proposal of a methodology to obtain highly accurate results in weakly bound small-band gap systems, where the screening of the Coulomb interactions is substantial. The present coupled cluster benchmark value for the exfoliation energy of black-P is a reference for other electronic structure methods targeting this very challenging system. Furthermore, it naturally calls for an experimental measurement of this property.

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Supporting Information Available: Detailed specification of the computational and structural models, full compilation of results, and related discussion.

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