Effect of dispersion corrections on ab initio predictions of graphite and diamond properties under pressure

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There are several approaches to the description of van der Waals (vdW) forces within density functional theory. While they are generally found to improve the structural and energetic properties of those materials dominated by weak dispersion forces, it is not known how they behave when the material is subject to an external pressure. This could be an issue when considering the pressure-induced structural phase transitions, which are currently attracting great attention following the discovery of an ultrahard phase formed by the compression of graphite at room temperature. In order to model this transition, the functional must be capable of simultaneously describing both strong covalent bonds and weak dispersion interactions as an isotropic pressure is applied. Here, we report on the ability of several dispersion-correction functionals to describe the energetic, structural, and elastic properties of graphite and diamond, when subjected to an isotropic pressure. Almost all of the tested vdW corrections provide an improved description of both graphite and diamond compared to the local density approximation. The relative error does not change significantly as pressure is applied, and in some cases even decreases. We therefore conclude that the use of dispersion-corrected exchange-correlation functionals, which have been neglected to date, will improve the accuracy and reliability of theoretical investigations into the pressure-induced phase transition of graphite.

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I. INTRODUCTION

Diamond and graphite are two of the best known allotropes of carbon. While the former is known for its extreme hardness, making it a highly valuable industrial component in many applications, the latter can be classified as a soft material with uses in lubrication and pencil lead. The differing mechanical behavior can be related to their respective crystalline structures. The carbon atoms in a diamond lattice are $sp^3$ hybridized in a tetrahedral geometry. This isotropic bonding configuration gives rise to an exceptional hardness. In contrast, graphite consists of planar sheets of $sp^2$ hybridized carbon atoms, with relatively weak dispersion forces holding the layers together. This anisotropic bonding means the layers can glide easily over each other, resulting in a macroscopic softness.

While graphite is the stable phase of carbon under normal conditions, the free-energy difference between it and diamond is only 30 meV [1]. Despite this, it is very difficult to convert graphite into diamond. Temperatures greater than 1700 K and pressures higher than 12 GPa are required to overcome the free-energy barrier preventing the spontaneous transition. The phase diagram of solid carbon also includes nanotubes, fullerenes, and amorphous $sp^2$ and $sp^3$ bonded carbon.

Several other phases emerge upon the application of an external pressure, including a metastable, crystalline, superhard, and transparent phase which is formed by the compression of graphite at room temperature [2–8]. The exact structure of this material is under considerable debate. Structure prediction methods, such as minima hopping, evolutionary algorithms, transition path sampling, and particle-swarm optimization, have suggested several contenders, including body-centered tetragonal $C_{4}$-carbon [9], orthorhombic $O$-carbon [10], W-carbon [10], Z-carbon [11], and monoclinic $M$-carbon [12,13], amongst others [14–17].

Those structure prediction methods based on first-principles density functional theory (DFT) generally employ standard local or semilocal approximations to the exchange-correlation energy in order to describe the electronic structure. However, such methods are inherently unable to describe the nonlocal dispersion interactions which dominate the interlayer binding of the starting material, graphite. While the local-density approximation (LDA) gives structural parameters which agree with experiment [18,19], this is a fortuitous agreement that masks an incomplete description of the interlayer van der Waals (vdW) interaction [20]. The generalized gradient approximation (GGA) fails to predict any graphite interlayer characteristics correctly, including its interlayer distance, binding energy, elastic constants, and phonon dispersions [21,22]. Thus, neither LDA nor GGA are suitable for an accurate description of graphite under pressure.

Mao et al. showed that the room-temperature (RT) compression of graphite caused approximately half of its $\pi$ bonds to convert to $\sigma$ bonds, with the other half remaining as $\pi$ bonds [6]. Therefore, in order to correctly describe
pressure-induced transitions of graphite on the atomic scale, one needs to be capable of simultaneously describing both strong covalent bonds (sp² and sp³) and weak dispersion interactions. Several functionals have been developed to improve the description of dispersion interactions in layered materials, with good results [23–31]. The effect of those functionals developed to describe vdW binding have also been applied to diamond and other ionic or semiconducting solids. In the considered cases, an improved agreement with experimental data has been found [32–38].

However, few first-principles calculations go beyond a determination of the equilibrium properties at zero external pressure. Yu et al. determined the structural properties of diamond and graphite under an applied pressure using the semiempirical correction of Grimme [39]. In this study, we extend this investigation to determine how well more sophisticated vdW-corrected functionals describe both AB-stacked hexagonal graphite and cubic diamond under an applied pressure. We determine their structural and elastic properties as well as how the stacking sequence of the carbon layers in graphite, namely hexagonal AB, rhombohedral ABC, and hexagonal AA, depends on the applied pressure. As the ultimate goal is to perform large-scale, finite-temperature simulations of the phase transition using ab initio molecular dynamics, it is important that a modest computational expense is maintained. For this reason, we restrict our investigation to six different vdW corrected functionals which are of reasonable computational cost, and do not consider more advanced functionals such as the many-body dispersion energy method of Tkatchenko et al. [40,41]. The main details of the employed functionals will be outlined in the following section.

II. THEORETICAL METHODS

A. Van der Waals functionals

We consider four different functionals which account for the dispersion interaction via a pair-wise additive correction to the total energy, namely, the semiempirical methods developed by Grimme (PBE+D3) [42], both with and without Becke-Johnson (BJ) damping (PBE+D3+BJ) [43] and two nonempirical methods developed by Tkatchenko and Scheffler: the standard method (PBE+TS) [44] and with the inclusion of a self-consistent screening (PBE+TS+SCS) [40].

In these functionals, the total energy \( E_{\text{total}} \) can be expressed as follows:

\[
E_{\text{total}} = E_{\text{KS-DFT}} + E_{\text{disp}},
\]

(1)

where \( E_{\text{KS-DFT}} \) is the conventional Kohn-Sham DFT energy and \( E_{\text{disp}} \) is the energy correction due to the dispersion interaction.

For the two Grimme methods, \( E_{\text{disp}} \) takes the form of a damped atom-pair-wise additive correction, such that

\[
E_{\text{disp}} = -\frac{1}{2} \sum_i \sum_j \frac{C_{6,ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij}),
\]

(2)

where \( C_{6,ij} \) is the dispersion coefficient for atom pair \( ij \) which depends on the local geometry via the coordination number of the atoms and \( R_{ij} \) is the distance between them. The damping term \( f_{\text{damp}} \) is to ensure that the potentials do not diverge at short distances. PBE+D3+BJ applies a correction to the damping function of PBE+D3 to ensure the dispersion energy approaches a constant value at small \( R \).

The two functionals developed by Tkatchenko and Scheffler, on the other hand, include the dispersion interaction as pair-wise potentials proportional to the rescaled polarizabilities of the free atoms. These are obtained from self-interaction corrected time-dependent DFT calculations [44]. The updated PBE+TS+SCS functional further accounts for electrodynamic response effects by solving the self-consistent screening (SCS) equation of electrodynamics for a dipole field of quantum harmonic oscillators [40].

We also consider two vdW functionals (optB86b [45] and rev-vdW-DF2 [46]) which, rather than account for vdW interactions via an additive correction to the total energy, include a nonlocal correlation energy that encompasses the long-range interactions. Here, the exchange correlation energy is defined as

\[
E_{\text{xc}} = E_{\text{GGA}}^{\text{XC}} + E_{\text{LDA}} + E_{\text{nl}},
\]

(3)

where \( E_{\text{GGA}}^{\text{XC}} \) is the GGA exchange energy and \( E_{\text{LDA}} \) is the local correlation within LDA. The remaining term, \( E_{\text{nl}} \), is a nonlocal correlation energy based on a model response function of interacting electron densities [47]. In the original formulation of Dion et al., the exchange energy was that of Perdew-Burke-Ernzerhof (revPBE) [48]. However, it was found to consistently overestimate equilibrium separations for the S22 benchmark set of molecular duplexes [49]. The optB86b method of Klimeš et al. replaces revPBE with a version of the B86b exchange functional [50] which was optimized by fitting to the S22 data set. A substantial improvement in accuracy was achieved [32,45]. We also employ the rev-vdW-DF2 functional developed by Hamada [46] which uses a revised B86b exchange functional together with the nonlocal correlation functional of vdw-DF2 [51]. An improved performance for a wide range of materials, including graphite and other layered materials, was found.

However, it is not clear how transferable this category of functionals are to systems beyond those for which they were designed. For example, they were shown to achieve good agreement for some systems including graphite and diamond [32,35], but to behave poorly when applied to the intralayer thickness of a variety of layered materials [26].

B. Computational details

Kohn-Sham DFT calculations were carried out using the projector augmented wave method [52] as implemented in VASP-5.3 [53–57]. Brillouin-zone integration was carried out using the Monkhorst-Pack method [58]. Convergence tests found that a cutoff energy of 1000 eV and a \( 23 \times 23 \times 11 \) k-point grid are required to describe AB-stacked graphite. The diamond structure was converged using a \( 9 \times 9 \times 9 \) k-point mesh. Structural optimizations were performed using the conjugate-gradient algorithm until the forces smaller than 1 meV/Å were achieved.

To obtain bulk properties, the total energies were calculated for a set of volumes corresponding to an increased isotropic pressure ranging between 0 and 30 GPa. Energy-volume data sets were then fitted using the Murnaghan equation of state.
TABLE I. Bulk properties of graphite and diamond at 0 GPa. MARE is defined in Eq. (5) using three descriptors for graphite \( (a_0, c_0, \text{and } B_0) \) and two descriptors for diamond \( (a_0 \text{ and } B_0) \). For the case of graphite, the data are compared to the experimental data taken at 4.2 K. For the case of diamond, the theoretical data are compared to experimental data taken from Ref. [65], which has already been corrected for thermal expansion and zero-point motion.

<table>
<thead>
<tr>
<th>Functional</th>
<th>( a_0 (\text{Å}) )</th>
<th>( c_0 (\text{Å}) )</th>
<th>( c_0/a_0 )</th>
<th>( B_0 ) (GPa)</th>
<th>MARE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>2.447</td>
<td>6.652</td>
<td>2.719</td>
<td>25.5</td>
<td>9.2</td>
</tr>
<tr>
<td>PBE+D3</td>
<td>2.465</td>
<td>6.965</td>
<td>2.825</td>
<td>23.2</td>
<td>12.7</td>
</tr>
<tr>
<td>PBE+D3+BJ</td>
<td>2.465</td>
<td>6.745</td>
<td>2.736</td>
<td>30.4</td>
<td>4.7</td>
</tr>
<tr>
<td>PBE+TS</td>
<td>2.459</td>
<td>6.690</td>
<td>2.721</td>
<td>53.5</td>
<td>17.9</td>
</tr>
<tr>
<td>PBE+TS+SCS</td>
<td>2.462</td>
<td>6.707</td>
<td>2.725</td>
<td>36.1</td>
<td>1.4</td>
</tr>
<tr>
<td>rev-vdW-DF2</td>
<td>2.464</td>
<td>6.608</td>
<td>2.682</td>
<td>44.7</td>
<td>9.7</td>
</tr>
<tr>
<td>optB86b</td>
<td>2.466</td>
<td>6.620</td>
<td>2.685</td>
<td>33.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Expt. [63] (4.2 K)</td>
<td>2.459</td>
<td>6.672</td>
<td>2.713</td>
<td>34.9</td>
<td>1.4</td>
</tr>
<tr>
<td>Expt. [64] (RT)</td>
<td>2.462</td>
<td>6.707</td>
<td>2.724</td>
<td>34-42</td>
<td></td>
</tr>
</tbody>
</table>

The ground-state structural properties of both graphite and diamond at 0 GPa are presented in Table I for LDA and the six considered dispersion-corrected functionals and compared to available experimental data. In order to determine the quality of the performance of different functionals in comparison with experiment over a variety of different descriptors such as lattice constants and bulk moduli, we define the mean absolute relative error (MARE) achieved by a functional as

\[
\text{MARE} = \frac{100}{n} \sum_{t=1}^{n} \left| \frac{\xi_{\text{expt}} - \xi_{\text{theo}}}{\xi_{\text{expt}}} \right|, \tag{5}
\]

where \( n \) is the number of descriptors being considered, \( \xi_{\text{expt}} \) is the experimental value of the descriptor, and \( \xi_{\text{theo}} \) is its theoretical value.

We find that all of the vdW-inclusive functionals give an improvement over LDA when considering the in-plane lattice constant of graphite, \( a_0 \); while LDA underestimates it by 0.5% compared to the low-temperature experimental value, each of the vdW functionals gives errors of less than 0.3%.

Mounet and Marzari calculated the effects of zero-point motion on the structural properties of graphite, and found that the \( a_0 \) lattice constant increases by 0.0074 Å [22]. In this case, the contribution was determined using the PBE functional and the experimental \( c/a \) ratio of graphite. However, we find that the zero-point energy varies by less than 1.3% when calculated with LDA, TS+SCS, and the MBD (at 0.17 meV/C). Similarly, Zhang et al. found that the effect of the specific functional on the zero-point energy was negligible when considering a database of bulk solids [38]. We find that the vdW-corrected functionals actually increase in error compared to LDA when the contribution of zero-point motion is included. The error associated with the in-plane lattice constant as determined by the LDA functional is 0.2% when corrected for zero-point motion, while all other functionals overestimate the \( a_0 \) by up to 0.6%. Nonetheless, these errors are relatively small and so we can conclude that all of the considered vdW functionals describe \( a_0 \) well.

Some vdW-inclusive functionals perform worse than LDA in describing the out-of-plane lattice parameter of graphite, \( c_0 \). In particular, the PBE+D3 functional overestimates \( c_0 \) by 4.4% compared to an error of 0.3% in LDA. The best performing functionals are those of Tkatchenko and Scheffler, with errors of less than 0.3% (0.5%) for PBE+TS (PBE+TS+SCS). The PBE+D3+BJ functional gives an error of 1.1%, while the two nonlocal functionals (rev-vdW-DF2 and optB86b) both underestimate \( c_0 \) by 1% and 0.8%, respectively. If zero-point motion is included to the extent determined by Mounet and Marzari (3%), those functionals which underestimated the \( c_0 \) lattice constant all improve with respect to experiment (i.e., LDA and the two nonlocal functionals) while those functionals which overestimate the lattice constant all increase in error by 0.3%. As a result, LDA is in fact found to fortuitously reproduce the experimental value exactly.
The agreement between theory and experiment is not as close when considering the bulk modulus. LDA fails to reproduce the experimental value, underestimating it by approximately 27%. PBE+D3 gives a similarly large error of 33%. The inclusion of BJ damping reduces this error to 13%. The best performance across all descriptors is given by PBE+TS, which both give results within the experimental error range of approximately 27%. The largest error is given by the PBE+TS+SCS functional, on the other hand, describes graphite as a much harder material than experimentally found, with a bulk modulus of 53.5 GPa, an overestimation of over 50%. This is in agreement with previous work [24]. PBE+D3+BJ functional also performs poorly, with an error of 28%. If we correct for zero-point motion, taking an increase in $B_0$ of approximately 1 GPa [22], the best performing functional is that of PBE+TS+SCS with an error of only 0.6%.

In fact, the best performance across all descriptors is given by PBE+TS+SCS and optB86b, with a MARE value of 1.4%, followed by the PBE+D3+BJ (4.7%) functional. These three functionals remain the best performers when zero-point corrections are taken into account.

Turning now to diamond, all functionals perform well in the description of the bulk lattice constant. The smallest error is again given by LDA (an underestimation of 0.2%). The vDW-corrected functionals all overestimate the lattice constant, but the error is never larger than 0.7% (that given by the two nonlocal functionals.) In this case, the lattice constant was compared to an experimental value of 3.543 Å which has been corrected for both thermal expansion at room temperature and zero-point motion [65].

The four $C_6$-corrected functionals are found to reduce the error associated with the bulk modulus of diamond compared to LDA, from 5.4% to less than 0.7%. The bulk modulus as determined with rev-vdW-DF2 and optB86b is underestimated by approximately 4%. Taking zero-point motion into account, which serves to reduce the bulk modulus by approximately 10 GPa at 0 K [22], the error in all of the vDW-corrected functionals increases by 2.3%.

The results presented here for ambient pressure agree with those presented in the literature [28–30,32,35]. Given that a good description of graphite and diamond is required simultaneously, we find that the PBE+TS+SCS is the best performing functional (with a MARE value of 1.0%), while both PBE+D3+BJ and optB86b also perform reasonably well (with MARE values between 1.9% and 2.6%). The large overestimation of the $c$ lattice constant of graphite using PBE+D3 and the large overestimation of the graphite bulk modulus using PBE+TS make these two functionals less accurate, with MARE values of just under 10%, and indeed, perform worse than LDA with a MARE of 6%. The inclusion of zero-point motion increases the error slightly, but the designation of PBE+TS+SCS, PBE+D3+BJ, and optB86b as the best performing functionals is not changed.

### B. Elastic properties

The elastic constants of graphite and diamond at 0 GPa as calculated with the different dispersion corrected functionals are presented in Table II and compared to experiment. Given that the values of some of the elastic constants are small, we define a different quality criterion to estimate the performance of the considered functionals. The mean absolute percentage error (MAPE) is defined as

$$\text{MAPE} = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{\xi_{\text{expt}} - \xi_{\text{theo}}}{\xi_{\text{expt}}} \right|,$$

where $n$ is the number of elastic constants considered, $\xi_{\text{expt}}$ is the experimental value, $\xi_{\text{theo}}$ is the theoretical value, and $\xi_{\text{expt}}$ is the reported experimental error, given by the corresponding error bars. Using this definition, theoretical values lying within the experimental error range give a MAPE between 0 and 1.

We find that the elastic constants of graphite are best described by the two nonlocal functionals, rev-vdW-DF2 and optB86b, which both give results within the experimental range. The largest error is given by the PBE+D3 functional (2.6%), followed by the two Tkatchenko-Scheffler functionals. PBE+D3+BJ and LDA give similar errors of approximately 1.5%.

For the case of diamond, LDA unsurprisingly yields substantial disagreement with experiment, with an absolute error of 7.4%. The best results are obtained with the $C_6$ corrected functionals, with errors of between 1.6% and 2.6%, while the nonlocal functionals perform somewhat worse with errors of almost 5%. However, these errors would represent the typical accuracy of elastic constants calculated with DFT.

Summarizing this section, we see that the best functionals for describing simultaneously the elastic constants of both graphite and diamond are the two Grimme functionals with...
In order to ensure a fair comparison, the compared to the experimental data obtained by Wang to 25 GPa for each of the considered functionals. This is then deviation of the calculated lattice parameter of graphite compared to experiment. The experimental data are taken from Ref. [64]. (d) The relative deviation of the calculated $c$ values from the experimental data. Note that in all cases the theoretical data have been corrected for thermal expansion and zero-point motion, as described in the text.

C. Pressure dependence

We now consider how these functionals behave when an external pressure is applied to both graphite and diamond. Figures 1(a) and 1(b) show how the $c$ lattice constant of graphite behaves as the external pressure is increased from 0 to 25 GPa for each of the considered functionals. This is then compared to the experimental data obtained by Wang et al. at room temperature [8]. In order to ensure a fair comparison, the theoretical data have been shifted to take zero-point motion and thermal expansion into account. The out-of-plane linear thermal expansion coefficient is $27 \times 10^{-6}$ K$^{-1}$ at room temperature [70]. This corresponds to an increase in the $c$ lattice constant of 0.05 Å as the temperature is raised to room temperature. The expansion of the $c$ lattice due to zero point motion is 0.02 Å [22]. As a result, the 0 K results are shifted by 0.07 Å and the results compared to the experimental data. Likewise, the theoretical data for the $a$ lattice constant have been shifted by 0.0064 Å, taking the linear expansion coefficient of $-1.5 \times 10^{-6}$ K$^{-1}$ at room temperature [70], as well as a zero-point expansion of 0.02 Å [22].

Note that above 19.2 GPa the experimental data showed evidence of a phase transition which was completed by 37 GPa. Due to the free-energy barrier, our theoretical calculations cannot reproduce this phase transition. Thus, beyond approximately 19 GPa we do not expect good agreement between the computational and experimental lattice constants. In this pressure range, experiment shows a decrease in both the $a$ and $c$ lattice parameters compared to the calculated values.

All of the functionals show the $c$ lattice parameter of graphite to reduce by approximately 1.3 Å when the pressure is increased from 0 to 25 GPa. This corresponds to a reduction in the interlayer distance of 0.65 Å.

As stated earlier, when corrected for zero-point motion, LDA predicts the $c$ lattice constant exactly at 0 GPa. However, the error increases with the application of pressure to just under 1% across a wide pressure window [Fig. 1(b)]. The best performance is achieved by the two nonlocal functionals which behave very similarly and give an error of no more than 0.2% across the whole pressure range. While PBE+D3+BJ gives an error of 1.7% at 0 GPa, this decreases to under 1% at higher pressures. The error of the two TS functionals initially increases with the application of pressure from about 1% to a maximum of more than 3.1% (2.3%) for PBE+TS (PBE+TS+SCS) at 6 GPa before decreasing. The PBE+D3 functional, while significantly overestimating the $c$ lattice constant at 0 GPa, performs better at higher pressures, reducing in error to about 2.5%.

One thing to note is that the thermal expansion and zero-point motion corrections have been applied uniformly across all pressures. However, it is possible that the effects of thermal expansion become less significant as the pressure is increased. Given the small errors involved here, it is likely that this would serve to reduce the error given by the vdW functionals at higher pressure.

All of the considered functionals reproduce the experimental in-plane lattice constant of graphite, with errors of no more than 0.5% for all functionals between 0 and 19 GPa. This can be seen in Figs. 1(c) and 1(d). In this case, the two TS functionals, which overestimate the experimental lattice constant by about 0.2% at all investigated pressures, perform slightly better than other functionals.

Next, we determine how the lattice constant of diamond behaves as a function of applied pressure. This is shown in Fig. 2 and compared to available experimental data [64], which was recorded at room temperature. Therefore, the theoretically determined lattice constant was increased by 0.024 Å, including a zero-point expansion of 0.013 Å [22].

The lattice constant of diamond is found to decrease linearly with the applied pressure. The errors achieved by each functional at ambient pressure remain approximately constant across the whole pressure window considered. LDA performs quite well, underestimating $a$ by 0.24%, which decreases slightly with the applied pressure. The PBE+TS.
The interlayer binding energy of graphite in the AB, AA, and ABC stackings are reported in Table III for each of the vdW functionals. For completeness, we now include the PBE+MBD functional, which includes nonlocal many-body dispersion (MBD) [33, 41]. This functional has previously been found to give a very accurate description of graphite [29]. The interlayer binding energy of the stacking $E_b^{\text{stacking}}$ is calculated as

$$E_b^{\text{stacking}} = -\frac{E_{\text{tot}} - N E_{\text{graphene}}}{nN},$$

(7)

where $E_{\text{tot}}$ is the total energy of graphite in a particular stacking sequence, $E_{\text{graphene}}$ is the total energy of an isolated graphene sheet, $N$ is the number of layers in the unit cell of each stacking (e.g., $N = 2$ for AB, $N = 3$ for ABC), and $n$ is the number of atoms in each layer. In addition, we report the energy difference between the chosen stacking and the ground-state AB structure $\Delta E$. This is defined as

$$\Delta E = E_b^{\text{stacking}} - E_b^{\text{AB stacking}}.$$  

(8)

The values calculated in this work are compared with available experimental data and with the random phase approximation (RPA) values, taken from Ref. [74]. Compared to the RPA values, the PBE+MBD functional method performs best with an MARE value of 6.0%, while the PBE+TS+SCS and PBE+D3+BJ functionals lead to a slight increase of the error to 7.3% and 10.2%, respectively. The PBE+TS functional without self-consistent screening performs the worst with an error of over 50%. These results are in good agreement with the reported structural and bulk properties since larger binding energies are associated with larger bulk moduli and smaller $c/a$ ratios.

We find that the energy difference between the ABC and the AB stackings are approximately 0.1 meV. While such small values are in agreement with experiment, which reports stacking fault energies of 0.09 meV/atom [75], the exact value is below the accuracy of our DFT methods. All of the considered functionals predict that AB-stacked graphite has a lower energy than ABC-stacked graphite, apart from PBE+TS+SCS which predicts that ABC is the ground-state structure. Given that the two stackings are so close in energy, it is common that DFT methods fail to predict comprehensively the correct ground state. Other factors, not considered here,
may also have to be taken into account, including the role of phonons.

It is possible that the stacking sequence of graphite could be influenced by an applied pressure, which in turn could be part of the phase transition pathway. To address this issue, we determined the difference in enthalpy between AB- and both ABC- and AA-stacked graphite as a function of applied pressure with the three functionals that perform best in describing graphite, namely, PBE+D3+BJ, PBS+TS+SCS, and optB86b, as well as PBE+MBD and LDA. The results are shown in Fig. 3. We find that while the application of pressure stabilizes AB-stacked graphite with respect to AA-stacked graphite, at a rate of approximately $-2.2 \text{ meV/GPa}$, the enthalpy difference between AB and ABC graphite remains minuscule, with differences of no more than $1.5 \text{ meV}$ over the entire pressure range considered. All four functionals behave similarly, with the greatest (least) stabilization achieved by the LDA (PBE+TS+SCS) functional.

IV. CONCLUSION

We investigated the ability of six different dispersion-corrected exchange correlation functionals to describe the structural and energetic properties of graphite and diamond as a function of an applied pressure. We included four functionals which include vdW interactions as an additive correction together with two functionals which include a nonlocal correlation term.

When considering the lattice constants, bulk moduli and elastic constants of both graphite and diamond, as well as the interlayer binding energy of graphite, we find that the best performing functional across all descriptors is PBE+TS+SCS with a combined error of just 2.2%. This is followed by the semiempirical PBE+D3+BJ functional with an error of 4.3%. The two nonlocal functionals give a combined error of between 6% and 7%. Primarily due to the significant overestimation of the $c$ lattice constant of graphite, the combined error of PBE+D3 is high, at 8.6%. The overestimation of both the graphite bulk modulus and interlayer binding energy means that the PBE+TS functional performs overall worse that LDA, with a combined mean absolute error of 13.7% compared to 9.2%.

This is the case at $P = 0 \text{ GPa}$, and the relative error to experiment does not change significantly upon the application of an isotropic pressure when considering the structural parameters. This is particularly the case for diamond, and in fact the error decreases slightly when compressing graphite.

Finally, we find that an isotropic pressure stabilizes AB-stacked graphite relative to AA-stacked graphite at a rate of $-2.2 \text{ meV/GPa}$ over the pressure range considered. In contrast, the relative energy of AB- and ABC-stacked graphite is in the range of $1.5 \text{ meV}$ over the entire pressure range considered, regardless of the dispersion correction used.

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