

Exploring interlayer coupling in the twisted bilayer PtTe₂Jeonghwan Ahn^{1,*}, Seoung-Hun Kang^{1,*}, Mina Yoon¹, and Jaron T. Krogel^{1,†}*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

(Received 17 April 2024; accepted 26 July 2024; published 16 August 2024)

We have investigated interlayer interactions in the bilayer PtTe₂ system, which influence the electronic energy bands near the Fermi level. Our diffusion Monte Carlo (DMC) calculations for the high-symmetry bilayer stackings (AA, AB, AC) manifest distinct interlayer binding characteristics among the stacking modes by revealing significantly different interlayer separations depending on the stacking, which is critical to understanding the interlayer coupling of the twisted bilayers consisting of various local stacking arrangements. Furthermore, a comparison between the interlayer separations obtained from DMC and density functional theory (DFT) shows that meta-generalized gradient approximation (GGA)-based van der Waals–DFT results agree with DMC for different layer stackings, including twisted bilayers, but only the ground-state AA stacking matches well with GGA-based DFT predictions. This underscores the importance of accurate exchange-correlation potentials even for capturing the stacking-dependent interlayer binding properties. We further show that the variability in DFT-predicted interlayer separations is responsible for the large discrepancy of band structures in the 21.79° twisted bilayer PtTe₂, affecting its classification as metallic or insulating. These results demonstrate the importance of obtaining a correct description of stacking-dependent interlayer coupling in modeling delicate bilayer systems at finite twists.

DOI: [10.1103/PhysRevResearch.6.033177](https://doi.org/10.1103/PhysRevResearch.6.033177)

I. INTRODUCTION

The nature of interlayer coupling is pivotal for two-dimensional (2D) layered materials since layer stacking has unveiled emergent features never seen in their single-layer form. Several stacking fashions when layering 2D materials allow us to explore their properties by manipulating stacking configurations away from the natural ground state [1–3], which leads to weakened interlayer coupling within the system. Subtle metastability arising from altering interlayer coupling enriches the correlated electronic phases in 2D materials, as exemplified by different topological properties depending on the stacking fashions [4–8]. These characteristics underscore the key role of interlayer coupling in understanding the properties of 2D layered materials.

Among the various layered materials, PtTe₂ has attracted a great deal of attention due to the presence of the strong interlayer coupling resulting in its intriguing electronic properties, such as topological semimetals [9,10] and the highest electrical conductivity at room temperature among metallic transition metal dichalcogenides (TMDs) [11,12]. Interestingly, an insulating single-layer PtTe₂ undergoes a transition to a semimetallic bilayer structure and maintains its semimetallicity up to the bulk structure [13] as a consequence of the interlayer hybridization between Te-*p_z* orbitals leading

to significant band gap reduction when forming the layered structures [14] (see also Fig. 1 in the Supplemental Material [15]), which is also well understood in other noble TMDs of PtS₂ [16] and PtSe₂ [17]. This highlights the importance of the interactions between layers in PtTe₂. Furthermore, the interlayer coupling is predicted to be controlled by a lateral shift of the upper layer with respect to the bottom layer, prospecting its potential uses in technologies like spintronics [18] and ferroelectrics [19].

More recently, the interlayer coupling of twisted systems in 2D layered materials has been studied intensively, as the twist gives rise to an additional degree of freedom to promote correlated phenomena of the system. The twisted layers are structured by the various stacking domains ranging from the most to least stable arrangements, with each local domain having different interlayer coupling effects. The presence of low stability local stackings in the twisted system weakens the interlayer interactions overall as the interlayer separation increases relative to the untwisted ground-state stacking. The degree of interlayer coupling thus evolves as a function of the twist angle [20–22], and the tunable interlayer coupling in the twisted bilayer systems opens a possibility to manipulate the properties of materials by twist angles such as exciton dynamics dependent on twist angles in MoSe₂/WSe₂ heterostructures [23]. Moreover, for PtTe₂, the way the layers interact is considered a mix of different forces originating from not only van der Waals (vdW) interactions but also the interlayer hybridization between the tellurium atoms in neighboring layers in addition to the possibility for metallic bonding. The complexity of the interactions alongside the structural features of twisted bilayer PtTe₂ makes it challenging for theory to accurately describe interlayer interactions in bilayer PtTe₂.

*These authors contributed equally to this work.

†Contact author: krogelj@ornl.gov

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

The challenges in modeling interlayer interactions are manifested in density functional theory (DFT) calculations, showing a notable difference in the interlayer distances for PtTe₂ [18] and its cousin materials of PtS₂ [16,24] and PtSe₂ [25,26]. As the interlayer distance is understood as a crucial parameter to directly tune the interlayer coupling [20,23], this variation, alongside the lack of experimental measurements for the bilayer structure of PtTe₂ makes choosing reliable DFT exchange-correlation functionals difficult. The many-body diffusion Monte Carlo (DMC) method, which can describe all types of bonding equally by explicitly incorporating the interactions between electrons, has been shown to overcome the challenges in describing complicated interlayer interactions. DMC has been utilized as a reliable reference, especially when there are no experimental data available for 2D layered materials [27–32]. This has led us to employ DMC to assist in choosing the most reliable exchange-correlation functionals within DFT to further enable broader studies of twisted PtTe₂ systems.

In this paper, we investigate interlayer interactions in bilayer PtTe₂ using both DFT and DMC calculations. A comparison between the interlayer distances obtained from DMC and various DFT calculations shows that the r²SCAN-based vdW functional results match DMC closely for different layer arrangements, including twisted bilayers. Generalized gradient approximation (GGA)-based calculations, however, only match well for one specific arrangement (the ground-state stacking) and show a wide range of layer distances for others with direct impacts on the predicted properties of the system. This inconsistency highlights the necessity to accurately model how layers interact across a variety of different stacking arrangements. This need is acute for twisted bilayers, which consist of various local stacking arrangements where the interlayer interactions differ significantly.

II. METHODOLOGY

We have performed the DFT calculations using VASP [33,34]. The projector augmented-wave pseudopotentials [35,36] for Pt and Te atoms were used to solve the Kohn-Sham equations by incorporating spin-orbit coupling effects. A plane-wave cutoff was set to 400 eV, and a primitive Brillouin zone was sampled with a $12 \times 12 \times 1$ ($12 \times 12 \times 8$) Monkhorst-Pack [37] k mesh for the bilayer and monolayer (bulk). The structural optimizations were done with a force threshold of 5×10^{-3} eV/Å, while electronic convergence was achieved with a threshold of 10^{-6} eV. To avoid spurious interactions between periodic images, a vacuum distance for the monolayer and bilayer is set to be 30 Å along the perpendicular direction to the PtTe₂ plane. In this paper, we consider self-consistent vdW functionals with different combinations of GGA exchanges and nonlocal correlation functionals such as vdW-optB86b [38], vdW-optB88 [39], vdW-DF2 [40], rev-vdW-DF2 [41], and rVV10 [42] as well as dispersion-corrected schemes including PBE + D3 [43], and PBE + MBD [44]. Furthermore, vdW functionals in combination with the meta-GGA functional, which additionally incorporates the local kinetic energy density term into the exchange part, such as r²SCAN + rVV10 [45], r²SCAN + D3,

and r²SCAN + MBD are considered, which allows us to discuss the importance of the semilocal part in the vdW-DFT calculations.

Our fixed-node DMC calculations were performed with the QMCPACK package [46,47]. We used a trial wave function of the Slater-Jastrow form [48] to incorporate many-body correlation effects into the Jastrow factors. In this paper, we considered electron-ion, electron-electron, and electron-electron-ion correlation effects described by 1-, 2-, and 3-body Jastrow factors, respectively. The Slater determinant comprised the PBE orbitals by solving the Kohn-Sham equations [49] with QUANTUM ESPRESSO [50]. The corresponding DFT calculations were performed with a plane-wave cutoff of 400Ry and $18 \times 18 \times 1$ Monkhorst-Pack k -point mesh [37] for the monolayer and bilayer structures using a norm-conserving potential with pseudovalence state of $5s^2 5p^6 6s^1 5d^9$ for the Pt atom, and the one developed within the ccECP scheme [51,52] for the Te atom, which were utilized in our previous DMC studies involved with these atomic species [32,53–55]. The one-body size effects were eliminated through the twist-averaged boundary conditions [56], and 36, 16, and 9 twist angles were utilized for three different supercell sizes of $2 \times 2 \times 1$, $3 \times 3 \times 1$, and $4 \times 4 \times 1$, respectively. The two-body size effects were mitigated by the extrapolation to the thermodynamic limit ($N = \infty$) by linear fit with the twisted-averaged total energies of three different supercells (see Fig. 2 in the Supplemental Material [15]). The Jastrow parameters were optimized through variational Monte Carlo calculations based on the linear method proposed by Umrigar *et al.* [57], while subsequent DMC calculations were carried out using a conservative time step of $\tau = 0.005 \text{ Ha}^{-1}$ in combination with size-consistent T moves for variationally estimating the nonlocal term of pseudopotentials as imaginary time projection proceeded [46].

III. RESULTS

A. DMC benchmark of bulk PtTe₂

Figure 1(a) shows that the crystal structure of bulk PtTe₂ consists of a single layer of PtTe₂ structured in three atomic layers. This structure features a TMD, each transition metal layer sandwiched between two chalcogen atom layers, forming an octahedral unit of 1T structure. This layered material has an AA-stacking configuration in its bulk structure, confirmed through experimental observations [9,13]. Figure 1(c) presents interlayer separations computed with several different DFT exchange-correlation functionals in comparison with experiment [9,13] for bulk PtTe₂. From this, we first observed that several DFT functionals like r²SCAN + rVV10, r²SCAN + D3, r²SCAN + MBD, vdW-optB86b, vdW-optB88, rev-vdW-DF2, rVV10, and PBE + MBD produced results within the range of the experiments. In contrast, the PBE + D3 and vdW-DF2 calculations showed larger deviations from these values. The largest deviation can be understood by the nonoptimized position of the Pauli wall in its exchange functional [39], leading to too-repulsive energy at short separations for the metallic systems [39,58,59]. The vdW functionals that improve exchange functionals from vdW-DF2, such as vdW-optB86b, vdW-optB88,

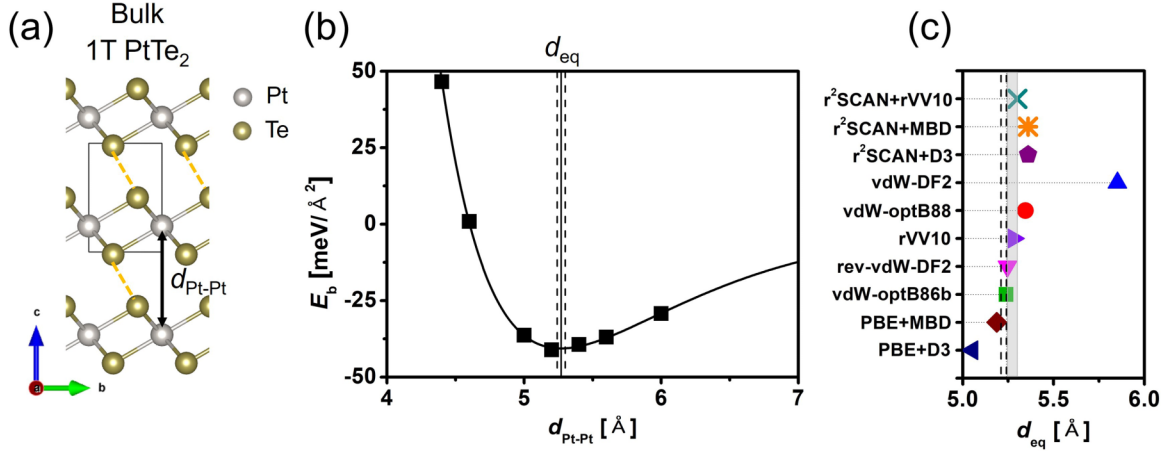


FIG. 1. (a) Side view of the crystal structure of bulk PtTe₂. The primitive cell is denoted by a black rectangle, and the corresponding interlayer separation is denoted by $d_{\text{Pt-Pt}}$. (b) Diffusion Monte Carlo (DMC) interlayer binding curve for bulk PtTe₂ computed with a $3 \times 3 \times 2$ supercell. The equilibrium interlayer separation d_{eq} is represented by a solid vertical line, while dotted vertical lines represent its statistical uncertainty. (c) Comparison between equilibrium interlayer separations from DMC, density functional theory (DFT), and experiment. The DMC data in (c) are represented by a gray-colored region reflecting the statistical uncertainty, while the experimental values are denoted by vertical dotted lines.

rev-vdW-DF2, and rVV10, are observed to show reasonable results with their deviation from the experimental values being $<3\%$. A dispersion-corrected scheme of PBE + D3 is known to show overestimation for the dispersion energy [60–62], and the better result from another corrected scheme of PBE + MBD might be attributed to the dispersion correction based on not only the distance but also the density [44]. The further improved results from PBE + D3 and PBE + MBD in combination with meta-GGA functionals (along with r²SCAN + rVV10) stem from the improved description of the interlayer hybridization effects for bulk PtTe₂. Next, we examine whether DMC can produce reasonable results comparable with bulk experimental values by computing the interlayer binding curve for bulk PtTe₂, as shown in Fig. 1(b). For this DMC calculation, we utilized a $3 \times 3 \times 2$ supercell containing 540 electrons where the in-plane lattice constant a is set to be the experimental value of 4.01 Å [13]. The equilibrium DMC interlayer distance is 5.27(3) Å, corresponding to the distance yielding maximum interlayer binding energy, which closely aligns with the experimentally observed distance of ~ 5.20 Å [63] to 5.24 Å [13], as shown in Fig. 1(c). This demonstrates the reliability of the DMC method for studying

interlayer interactions in layered PtTe₂ materials, which justifies its role of acting as a reference relative to DFT for the bilayer systems that lack experimental measurement for the structural parameters.

B. Discrepancies in DFT energetics and interlayer separations of high-symmetry bilayer stackings

We now analyze the bilayer PtTe₂ systems. One can consider three different high-symmetric stacking modes, namely, AA-, AB-, and AC-stacking modes, as displayed in Figs. 2(a)–2(c), respectively. These stacking modes can be identified in Fig. 2(d), which presents a contour map of relative total energies computed with r²SCAN + rVV10 for the lateral shift of the upper PtTe₂ layer with respect to the lower layer (the potential energy surface of relative lateral translations). We find that AA stacking is the lowest-energy configuration, and AC stacking corresponds to a very shallow local minimum in the stacking energy maps (a metastable state), with the energy difference from the ground-state structure being 3.5 meV/Å². In contrast, the AB stacking is the most unstable configuration. Note that the overall energy

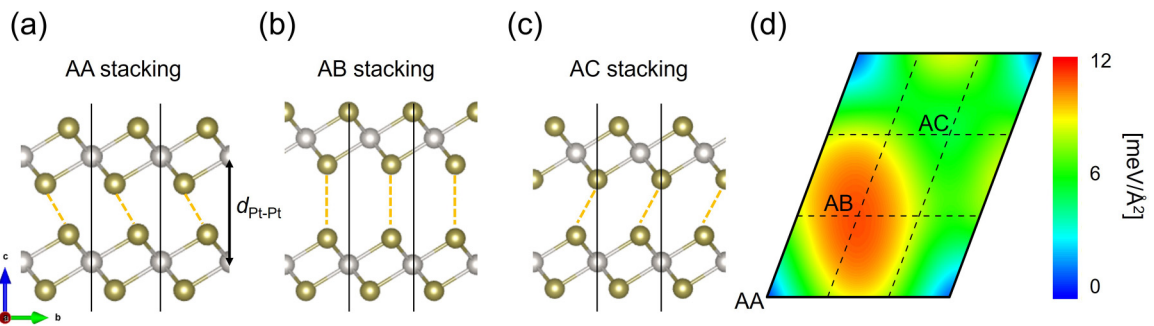


FIG. 2. Side view of the crystal structure for (a) AA-stacked, (b) AB-stacked, and (c) AC-stacked bilayer PtTe₂. The corresponding interlayer separation $d_{\text{Pt-Pt}}$ is denoted in (a). (d) Potential energy surface for the lateral translations of the upper PtTe₂ layer with respect to the lower one computed with r²SCAN + rVV10.

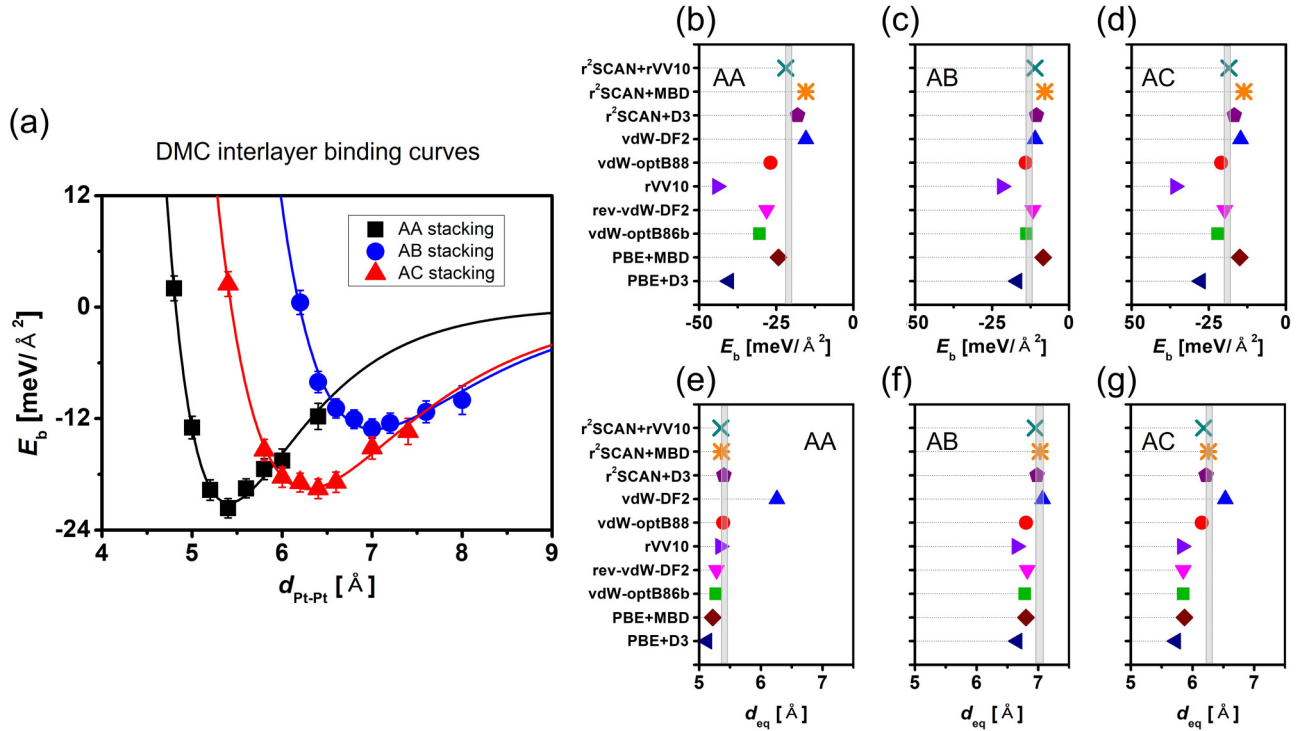


FIG. 3. (a) Diffusion Monte Carlo (DMC) interlayer binding curve for AA-, AB-, and AC-stacked bilayer PtTe₂ constructed with the finite-sized corrected DMC energies. The comparison between DMC and density functional theory (DFT) interlayer binding energies for (b) AA-stacking, (c) AB-stacking, and (d) AC-stacking modes, while the comparison of interlayer separations for AA-, AB-, and AC-stacked bilayer PtTe₂ are presented in (e)–(g). The DMC data in (b)–(g) are represented by a gray-colored region reflecting the statistical uncertainty.

ordering among the high-symmetry stacking modes is not affected by the choice of the DFT functional. Nevertheless, there are large quantitative inconsistencies in the energetics among different bilayer stacking modes, reflecting the different descriptions of the interlayer interactions arising from the metallic + vdW + hybridization type bonding in PtTe₂ depending on the DFT functional. Therefore, high-level benchmarking to the many-body DMC calculations is desirable to arrive at a trustworthy prediction of the stability of the bilayer structures with different stacking modes.

To this end, we performed the DMC calculations for AA-, AB-, and AC-stacked bilayer PtTe₂ as representative elements of stable, unstable, and intermediate stacking regions, respectively, to understand the interlayer coupling in twisted bilayer system. Figure 3(a) presents the DMC interlayer binding curves for three stacking modes, which were constructed with finite-sized corrected DMC energies extrapolated to the thermodynamic limit, as in Fig. 2 in the Supplemental Material [15]. This allows us to determine equilibrium interlayer binding energies for each stacking mode, which confirms AA stacking to be the most stable among the three symmetric stacking modes, as predicted in our DFT calculations discussed above. The interlayer binding energies for AB- and AC-stacking modes are higher than that of the AA stacking by 8(1) and 2(1) meV/Å², respectively. The DMC binding energies are compared with the DFT binding energies computed with several different vdW functionals for each stacking, as presented in Figs. 3(b)–3(d) and Table I in the Supplemental Material [15]. The comparison shows that the results from the r²SCAN-based functionals are consistently superior to

the GGA-based ones, which is attributed to a better description of the inhomogeneity of electron densities induced by the interplay between vdW interactions and interlayer hybridization effects where the exchange interaction would be integral. A description of the exchange interaction could be improved by incorporating the kinetic energy density into the semilocal exchange functionals in the meta-GGA functionals. However, considering the root mean square error (RMSE) for the energetics of r²SCAN + rVV10 (1.3 meV/Å²), which is nearly twice as accurate as the next-best-performing functional (r²SCAN + D3 with RMSE of 2.5 meV/Å²; see Table I in the Supplemental Material [15]), r²SCAN + rVV10 results best agree with DMC in predicting the binding energies for all stacking modes. This makes it robust even in predicting the relative energies among the bilayer structure with different stacking modes. The robustness of r²SCAN + rVV10 against r²SCAN + D3 and r²SCAN + MBD might be due to whether vdW interactions are involved in obtaining converged electron densities in the self-consistency procedure because r²SCAN could capture only hybridization effects.

Next, let us consider interlayer separations, which characterize the nature of the interlayer coupling, for the symmetrically stacked and twisted bilayer PtTe₂ from the comparison between DMC and DFT results. The interlayer separation needs to be more carefully investigated than the interlayer binding energies because it is critically relevant to the electronic structures, especially near the Fermi level, which makes it a crucial factor that results in sensitive electronic properties. Figures 3(e)–3(g) display interlayer separations computed with DMC and DFT for AA-, AB-, and AC-stacked

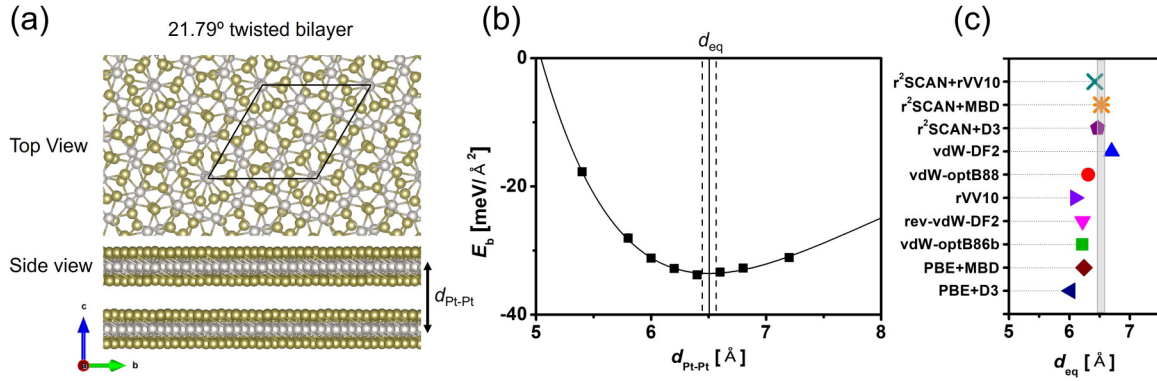


FIG. 4. (a) Top and side views of the crystal structure of 21.79° twisted bilayer PtTe_2 . The primitive unit cell is represented with the parallelogram enclosed by black lines, and the corresponding interlayer separation is denoted by $d_{\text{Pt-Pt}}$. (b) Diffusion Monte Carlo (DMC) interlayer binding curve for 21.79° twisted bilayer PtTe_2 computed with a $1 \times 1 \times 1$ supercell. The equilibrium interlayer separation d_{eq} is represented by a solid vertical line, while dotted vertical lines represent its statistical uncertainty. (c) Comparison of DMC and density functional theory (DFT) interlayer separations for 21.79° twisted bilayer PtTe_2 . The DMC data in (c) are represented by a gray-colored region reflecting the statistical uncertainty.

bilayer PtTe_2 (the corresponding data are tabulated in Table 2 in the Supplemental Material [15]). The DMC interlayer binding distance for the AA-stacking mode is found to be the shortest, followed by those of AC- and AB-stacking modes, with 5.41(5), 6.27(5), and 7.02(6) Å, respectively. The considerable variation in the bilayer separation distances suggests the characteristics of the interlayer coupling would be significantly different depending on the stacking modes, manifesting the strong interlayer coupling in the bilayer PtTe_2 system. Indeed, the interlayer separations for the most stable AA and the most unstable AB stackings correspond to the interlayer nearest-neighbor Te-Te distances of 3.50(5) and 4.24(6) Å, respectively. These distances are within a range from the sum of the covalent radii of Te atoms (2.76 Å) [64] to the vicinity of the sum of their vdW radii (4.12 Å) [65], suggesting that orbital hybridization effects are substantially involved in interlayer couplings in addition to the vdW interactions for the AA stacking, while the vdW interactions mainly characterize the interlayer coupling for the AB stacking. The interlayer hybridization of AA stacking is further evidenced by the agreement for the corresponding interlayer separations between DMC and semilocal functionals of PBE (5.36 Å) and $r^2\text{SCAN}$ (5.47 Å), in which the long-range vdW correlation is absent.

As shown in Figs. 3(e)–3(g) presenting the comparison between DMC and DFT results, one can see that $r^2\text{SCAN} + r\text{VV10}$, $r^2\text{SCAN} + \text{MBD}$, $r^2\text{SCAN} + \text{D3}$, vdW-optB88 , and $r\text{VV10}$ results agree with DMC for the AA-stacked bilayer. However, for the AB- and AC-stacking modes, only $r^2\text{SCAN}$ -based vdW functionals match with DMC, while vdW-optB88 and $r\text{VV10}$ separation distances become far away from the DMC values, including the rest of the DFT functionals that poorly describe the AA stacking. This indicates that the stacking-dependent interlayer coupling is similarly described with the DMC and the $r^2\text{SCAN}$ -based vdW functionals overall, possibly due to its improvement of the semilocal part in the vdW functionals, which highlights the importance of the role of semilocal exchange-correlation potential even in the prediction of the interlayer binding properties. More specifically, the discrepancy in the DFT interlayer separations is found to be largest for the AC stackings, followed by the AB

and AA stackings. Considering that the binding natures of AA and AB stackings turn out to be mainly characterized by interlayer Te- p_z hybridization and the vdW interactions, DFT is considered to have more limitations in describing the interlayer interactions, with both contributions being comparable with each other such as in the case of the AC stacking. This strongly suggests that the different degrees of discrepancy in the DFT interlayer separations depending on the stacking modes would still influence that of twisted bilayer PtTe_2 in light of its structural feature consisting of various local stacking domains, including AA-, AB-, and AC-like regions.

C. Discrepancies in DFT interlayer separations of twisted bilayer

To further examine the performance of candidate DFT functionals for a twisted system, we investigate twisted bilayer PtTe_2 with a twist angle of 21.79° from the AA stacking. It has the smallest moiré pattern among the twisted bilayer systems, namely, $p(\sqrt{7} \times \sqrt{7})$, as shown in Fig. 4(a). When constructing the DMC interlayer binding curves, as displayed in Fig. 4(b) for the 21.79° twisted bilayer, we used the $1 \times 1 \times 1$ unit cell containing 420 electrons. Figure 4(c) presents the optimized interlayer binding distance computed from DMC and DFT calculations. The DMC calculations find the equilibrium distances to be 6.52(6) Å, which falls between that of the AB and AC stackings. This is a consequence of the mixed stacking configurations from stable to unstable ones. In terms of interlayer separations, the 21.79° twisted bilayer is expected to show interlayer hybridization plus vdW characteristics that are slightly weaker than that of the AC stacking mode, underscoring the importance of the well-balanced description of interlayer hybridization and vdW interactions to simulate the twisted bilayer PtTe_2 accurately.

From the comparison between DMC and DFT results for the 21.79° twisted bilayer, as shown in Fig. 4(d), $r^2\text{SCAN}$ -based vdW functionals that are robust for each high-symmetry stacking mode also agree with the DMC interlayer separation for twisted bilayer PtTe_2 . As can be seen in Table II in the Supplemental Material [15], the RMSEs of interlayer

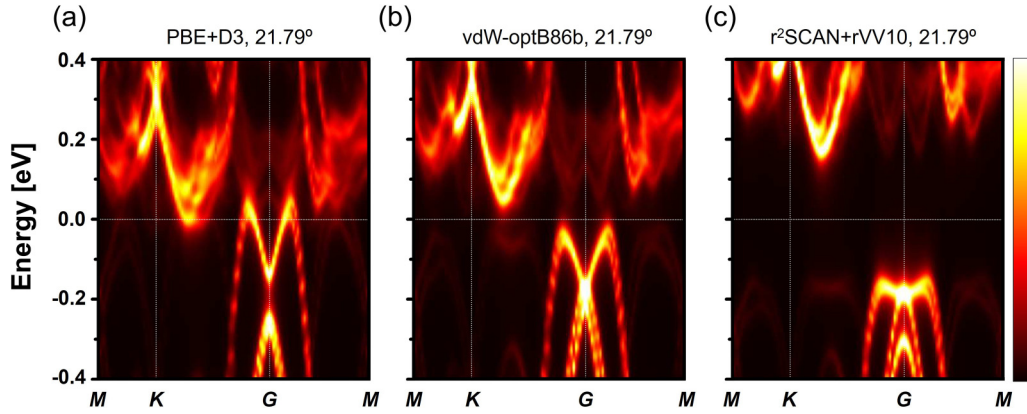


FIG. 5. Unfolded band structures of the 21.79° twisted bilayer PtTe_2 for primitive Brillouin zone of the 0° bilayer AA-stacked PtTe_2 using (a) PBE + D3, (b) vdW-optB86b, and (c) $r^2\text{SCAN} + r\text{VV10}$ with inclusion of spin-orbit coupling.

separations for the $r^2\text{SCAN} + r\text{VV10}$, $r^2\text{SCAN} + \text{D3}$, and $r^2\text{SCAN} + \text{MBD}$ functionals are found to be 0.05, 0.05, and 0.06 Å, respectively, which are over twice as accurate as the next-nearest functional (0.13 Å for vdW-optB88). However, in conjunction with the energetics discussed above, we conclude that $r^2\text{SCAN} + r\text{VV10}$ is the most reliable for simulating the PtTe_2 systems, even including twist, among the currently available vdW-corrected functionals. Interestingly, the discrepancy in the DFT interlayer separations for the 21.79° twisted bilayer is similarly patterned to that of the AB- and AC-stacking modes, which have interlayer separations closer to that of the twisted system as compared with AA stacking. From this fact, we understand the large discrepancy for the twisted bilayer to originate from larger discrepancies for the AB and AC stackings and not from the equilibrium AA-stacking mode. This highlights the importance of correctly describing the interlayer couplings varying with the stacking modes away from the ground-state AA stacking to include less stable configurations such as AB and AC stackings when it comes to understanding twisted bilayer systems. The large discrepancy for the twisted bilayer can also be understood in terms of its optimal DMC interlayer separation of 6.52(6) Å, where the contributions from the interlayer hybridization and vdW interactions are expected to be comparable. However, as discussed above, it turns out to be challenging to describe with the DFT calculations.

D. Impact of discrepancies in DFT interlayer separations on the electronic structures

Finally, we discuss the influence of the interlayer separations on the electronic structures for the bilayer PtTe_2 systems. Figure 5 displays the band structures of twisted bilayer PtTe_2 with a twist angle of 21.79° computed with PBE + D3, vdW-optB86b, and $r^2\text{SCAN} + r\text{VV10}$ using the geometries optimized with the respective functionals, which are unfolded to the primitive Brillouin zone of nontwisted bilayer PtTe_2 . The electronic structures are found to differ considerably depending on the functionals: PBE + D3 yields a semimetallic band structure, while vdW-optB86b and $r^2\text{SCAN} + r\text{VV10}$ predict the twisted bilayer to be an insulator with band gaps of 0.08 and 0.32 eV, respectively. The comparison implies a failure to predict the interlayer distances could result in

incorrect electronic structures, leaving uncertainty for its true electronic structure. The discrepancy in the band structures for the twisted bilayer is attributed to the huge discrepancy of the optimized interlayer separations, as seen in Fig. 4(d), because it governs the magnitude of the splitting between the antibonding and bonding states by the interlayer $\text{Te}-p_z$ hybridization that results in band gap reduction from the monolayer band gap (see Fig. 1 in the Supplemental Material [15]). Note that there is very small distortion (<0.03 Å) in the planar structures in the 21.79° twisted bilayer in any DFT calculations. Indeed, due to the same mechanism, AB and AC stackings also show noticeable differences in the band structures depending on the functional, as can be seen in Fig. 3 in the Supplemental Material [15]. However, in contrast with the cases of AB and AC, the computed band structures for the AA stacking hardly differ. This is attributed to the smallest spread of the DFT interlayer separation for the AA stacking, which is justified by the negligible difference in the band structures from different functionals when the structural degrees of freedom are held fixed (see Fig. 4 in the Supplemental Material [15]). This suggests that the interlayer separation itself is a more sensitive factor than the choice of the DFT functionals in determining the band structures of the PtTe_2 system. Consequently, the difference in the band structure for the twisted bilayer can also be considered to originate from the discrepancy of the high-symmetric bilayer stacking modes. This highlights again the significance of the stacking-dependent interlayer coupling driven by the significantly varying interlayer distance depending on the stacking mode to understand the twisted bilayer system, which would be particularly important for the system where the interlayer separations would lead to different electronic states such as the twisted bilayer PtTe_2 system.

IV. CONCLUSIONS

We have investigated interlayer coupling in bilayer PtTe_2 systems by carrying out both DMC and DFT calculations, which aid in understanding the strong sensitivities this system displays with respect to commonly chosen vdW functionals. Our analysis serves to inform the community regarding the most reliable DFT functionals for studying the twisted bilayer systems. To this end, we compared the interlayer

binding energies and separations between DMC and several different DFT functionals for three different high-symmetry bilayer stacking modes (AA, AB, and AC). From DMC, we find that the interlayer separations strongly depend on the stacking mode, reflecting different interaction characteristics among the stackings. The range of DMC-benchmarked stacking-dependent interlayer couplings is found to be well captured by only $r^2\text{SCAN} + r\text{VV10}$ for both energetics and interlayer separations, which makes it robust even in predicting the interlayer separations for the 21.79° twisted bilayer. This can be understood from the ability of $r^2\text{SCAN} + r\text{VV10}$ to correctly describe the interlayer couplings of all the local stacking modes that the twisted bilayer contains. Furthermore, we found differing degrees of discrepancy in the DFT interlayer separations depending on the stacking modes, with the largest discrepancies in interlayer separation and band structure appearing for the less stable AB and AC stackings. This behavior directly leads to a huge difference in the properties of the twisted bilayer. Our results underscore the significance of understanding the interlayer couplings of high-symmetry bilayer stacking modes beyond the ground-state configuration, including the less stable stackings that appear under twist.

In this respect, our DMC calculations play a guiding role in not only narrowing down large discrepancies among vdW-DFT functionals for systems with complicated interactions in PtTe_2 but also in providing comprehensive insight into critical ingredients to model the twisted bilayer system, namely, stacking-dependent interlayer coupling. It is revealed from the comparison between the GGA-based and meta-GGA-based vdW-DFT results against the DMC calculations that improving the semilocal exchange-correlation potentials provides a pathway to develop more sophisticated DFT functionals that capture the stacking-dependent interlayer interactions of complicated systems. Furthermore, $r^2\text{SCAN} + r\text{VV10}$, which we find to be the most reliable functional for the bilayer PtTe_2 system, shows promise to be utilized in further theoretical studies of PtTe_2 systems, such as twist-induced phase transitions which are of great current theoretical interest.

ACKNOWLEDGMENTS

Work performed by J.A. and J.T.K. (concept, DMC and DFT total energy calculations, data analysis, and manuscript writing) was supported by the DOE, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, as part of the Computational Materials Sciences Program and Center for Predictive Simulation of Functional Materials. The work performed by S.-H.K. and M.Y. (band unfolding calculations, data analysis, and manuscript writing) was supported by the U.S. DOE, Office of Science, National Quantum Information Science Research Centers, Quantum Science Center (S.-H.K.) and U.S. DOE, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division (M.Y.).

An award of computer time was provided by the Innovative and Novel Computational Impact on Theory and Experiment (INCITE) program. For this paper, we used resources of the Argonne Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract No. DE-AC02-06CH11357. We also used resources of the Oak Ridge Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract No. DE-AC05-00OR22725, and resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the DOE under Contract No. DE-AC02-05CH11231 using NERSC Award No. BES-ERCAP0028956.

This paper has been partially supported by the DOE. ORNL is managed by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 for the U.S. DOE. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this paper, or allow others to do so, for U.S. Government purposes. The U.S. Department of Energy (DOE) will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan [66].

-
- [1] Y. Cao, V. Fatemi, A. Demir, S. Fang, S. L. Tomarken, J. Y. Luo, J. D. Sanchez-Yamagishi, K. Watanabe, T. Taniguchi, E. Kaxiras *et al.*, Correlated insulator behaviour at half-filling in magic-angle graphene superlattices, *Nature (London)* **556**, 80 (2018).
 - [2] M. Vizner Stern, Y. Waschitz, W. Cao, I. Nevo, K. Watanabe, T. Taniguchi, E. Sela, M. Urbakh, O. Hod, and M. Ben Shalom, Interfacial ferroelectricity by van der Waals sliding, *Science* **372**, 1462 (2021).
 - [3] I. Hagymási, M. S. Mohd Isa, Z. Tajkov, K. Mártí, L. Oroszlány, J. Koltai, A. Alassaf, P. Kun, K. Kandrai, A. Pálkás *et al.*, Observation of competing, correlated ground states in the flat band of rhombohedral graphite, *Sci. Adv.* **8**, eabo6879 (2022).
 - [4] X. Qian, J. Liu, L. Fu, and J. Li, Quantum spin Hall effect in two-dimensional transition metal dichalcogenides, *Science* **346**, 1344 (2014).
 - [5] A. A. Soluyanov, D. Gresch, Z. Wang, Q. Wu, M. Troyer, X. Dai, and B. A. Bernevig, Type-II Weyl semimetals, *Nature (London)* **527**, 495 (2015).
 - [6] T.-R. Chang, S.-Y. Xu, G. Chang, C.-C. Lee, S.-M. Huang, B. Wang, G. Bian, H. Zheng, D. S. Sanchez, I. Belopolski *et al.*, Prediction of an arc-tunable Weyl fermion metallic state in $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$, *Nat. Commun.* **7**, 10639 (2016).
 - [7] H.-J. Kim, S.-H. Kang, I. Hamada, and Y.-W. Son, Origins of the structural phase transitions in MoTe_2 and WTe_2 , *Phys. Rev. B* **95**, 180101(R) (2017).
 - [8] S.-H. Kang, S. Jeon, H.-J. Kim, W. Ko, S. Cho, S. H. Kang, S. W. Kim, H. Yang, H. W. Kim, and Y.-W. Son, Reshaped Weyl fermionic dispersions driven by Coulomb interactions in MoTe_2 , *Phys. Rev. B* **105**, 045143 (2022).
 - [9] K. Zhang, M. Yan, H. Zhang, H. Huang, M. Arita, Z. Sun, W. Duan, Y. Wu, and S. Zhou, Experimental evidence for type-II Dirac semimetal in PtSe_2 , *Phys. Rev. B* **96**, 125102 (2017).

- [10] M. Yan, H. Huang, K. Zhang, E. Wang, W. Yao, K. Deng, G. Wan, H. Zhang, M. Arita, H. Yang *et al.*, Lorentz-violating type-II Dirac fermions in transition metal dichalcogenide PtTe₂, *Nat. Commun.* **8**, 257 (2017).
- [11] S. Hao, J. Zeng, T. Xu, X. Cong, C. Wang, C. Wu, Y. Wang, X. Liu, T. Cao, G. Su *et al.*, Low-temperature eutectic synthesis of PtTe₂ with weak antilocalization and controlled layer thinning, *Adv. Funct. Mater.* **28**, 1803746 (2018).
- [12] H. Xu, J. Wei, H. Zhou, J. Feng, T. Xu, H. Du, C. He, Y. Huang, J. Zhang, Y. Liu *et al.*, High spin Hall conductivity in large-area type-II Dirac semimetal PtTe₂, *Adv. Mater.* **32**, 2000513 (2020).
- [13] M.-K. Lin, R. A. B. Villaos, J. A. Hlevyack, P. Chen, R.-Y. Liu, C.-H. Hsu, J. Avila, S.-K. Mo, F.-C. Chuang, and T.-C. Chiang, Dimensionality-mediated semimetal-semiconductor transition in ultrathin PtTe₂ films, *Phys. Rev. Lett.* **124**, 036402 (2020).
- [14] L. Han, Y. Zou, Q. Zeng, X. Guan, B. Jia, Y. Gao, G. Liu, and L. Wu, Strong interlayer interaction in two-dimensional layered PtTe₂, *J. Solid State Chem.* **305**, 122657 (2022).
- [15] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevResearch.6.033177> for details of antibonding and bonding splitting in the AA-stacked bilayer, the $1/N$ extrapolation of the DMC supercell energies to the bulk limit, structural parameters optimized with DMC and DFT, and band structures depending on the stacking mode/functionals.
- [16] Y. Zhao, J. Qiao, P. Yu, Z. Hu, Z. Lin, S. P. Lau, Z. Liu, W. Ji, and Y. Chai, Extraordinarily strong interlayer interaction in 2D layered PtS₂, *Adv. Mater.* **28**, 2399 (2016).
- [17] Y. Zhao, J. Qiao, Z. Yu, P. Yu, K. Xu, S. P. Lau, W. Zhou, Z. Liu, X. Wang, W. Ji *et al.*, High-electron-mobility and air-stable 2D layered PtSe₂ FETs, *Adv. Mater.* **29**, 1604230 (2017).
- [18] J. Li, H. Jin, Y. Wei, and H. Guo, Tunable intrinsic spin Hall conductivity in bilayer PtTe₂ by controlling the stacking mode, *Phys. Rev. B* **103**, 125403 (2021).
- [19] H. Sheng, Z. Fang, and Z. Wang, Ferroelectric metals in 1T/1T'-phase transition metal dichalcogenide MTe₂ bilayers ($M = \text{Pt, Pd, and Ni}$), *Phys. Rev. B* **108**, 104109 (2023).
- [20] K. Liu, L. Zhang, T. Cao, C. Jin, D. Qiu, Q. Zhou, A. Zettl, P. Yang, S. G. Louie, and F. Wang, Evolution of interlayer coupling in twisted molybdenum disulfide bilayers, *Nat. Commun.* **5**, 4966 (2014).
- [21] W. Yan, L. Meng, Z. Meng, Y. Weng, L. Kang, and X.-a. Li, Probing angle-dependent interlayer coupling in twisted bilayer WS₂, *J. Phys. Chem. C* **123**, 30684 (2019).
- [22] H. Zheng, H. Guo, S. Chen, B. Wu, S. Li, J. He, Z. Liu, G. Lu, X. Duan, A. Pan *et al.*, Strong interlayer coupling in twisted transition metal dichalcogenide moiré superlattices, *Adv. Mater.* **35**, 2210909 (2023).
- [23] P. K. Nayak, Y. Horbatenko, S. Ahn, G. Kim, J.-U. Lee, K. Y. Ma, A.-R. Jang, H. Lim, D. Kim, S. Ryu *et al.*, Probing evolution of twist-angle-dependent interlayer excitons in MoSe₂/WSe₂ van der Waals heterostructures, *ACS Nano* **11**, 4041 (2017).
- [24] S. Ahmad, Strain and electric field dependent variation in electronic and thermoelectric properties of PtS₂, *Res. Phys.* **17**, 103088 (2020).
- [25] J. Li, S. Kolekar, M. Ghorbani-Asl, T. Lehnert, J. Biskupek, U. Kaiser, A. V. Krashenninnikov, and M. Batzill, Layer-dependent band gaps of platinum dichalcogenides, *ACS Nano* **15**, 13249 (2021).
- [26] L. Zhang, T. Yang, M. F. Sahdan, Arramel, W. Xu, K. Xing, Y. P. Feng, W. Zhang, Z. Wang, and A. T. S. Wee, Precise layer-dependent electronic structure of MBE-grown PtSe₂, *Adv. Electron. Mater.* **7**, 2100559 (2021).
- [27] E. Mostaani, N. D. Drummond, and V. I. Fal'ko, Quantum Monte Carlo calculation of the binding energy of bilayer graphene, *Phys. Rev. Lett.* **115**, 115501 (2015).
- [28] L. Shulenburger, A. D. Baczewski, Z. Zhu, J. Guan, and D. Tomanek, The nature of the interlayer interaction in bulk and few-layer phosphorus, *Nano Lett.* **15**, 8170 (2015).
- [29] H. Shin, J. Kim, H. Lee, O. Heinonen, A. Benali, and Y. Kwon, Nature of interlayer binding and stacking of sp - sp^2 hybridized carbon layers: A quantum Monte Carlo study, *J. Chem. Theory Comput.* **13**, 5639 (2017).
- [30] J. Ahn, I. Hong, Y. Kwon, R. C. Clay, L. Shulenburger, H. Shin, and A. Benali, Phase stability and interlayer interaction of blue phosphorene, *Phys. Rev. B* **98**, 085429 (2018).
- [31] J. Ahn, I. Hong, G. Lee, H. Shin, A. Benali, and Y. Kwon, Metastable metallic phase of a bilayer blue phosphorene induced by interlayer bonding and intralayer charge redistributions, *J. Phys. Chem. Lett.* **12**, 10981 (2021).
- [32] J. Ahn, I. Hong, G. Lee, H. Shin, A. Benali, J. T. Krogel, and Y. Kwon, Structural stability of graphene-supported Pt layers: Diffusion Monte Carlo and density functional theory calculations, *J. Phys. Chem. C* **127**, 18630 (2023).
- [33] G. Kresse and J. Hafner, *Ab initio* molecular dynamics for liquid metals, *Phys. Rev. B* **47**, 558 (1993).
- [34] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [35] P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B* **50**, 17953 (1994).
- [36] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* **59**, 1758 (1999).
- [37] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B* **13**, 5188 (1976).
- [38] J. Klimeš, D. R. Bowler, and A. Michaelides, Chemical accuracy for the van der Waals density functional, *J. Phys.: Condens. Matter* **22**, 022201 (2010).
- [39] J. Klimeš, D. R. Bowler, and A. Michaelides, van der Waals density functionals applied to solids, *Phys. Rev. B* **83**, 195131 (2011).
- [40] K. Lee, É. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, Higher-accuracy van der Waals density functional, *Phys. Rev. B* **82**, 081101(R) (2010).
- [41] I. Hamada, van der Waals density functional made accurate, *Phys. Rev. B* **89**, 121103(R) (2014).
- [42] R. Sabatini, T. Gorni, and S. de Gironcoli, Nonlocal van der Waals density functional made simple and efficient, *Phys. Rev. B* **87**, 041108(R) (2013).
- [43] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* **132**, 154104 (2010).
- [44] A. Tkatchenko, R. A. DiStasio, R. Car, and M. Scheffler, Accurate and efficient method for many-body van der Waals interactions, *Phys. Rev. Lett.* **108**, 236402 (2012).

- [45] J. Ning, M. Kothakonda, J. W. Furness, A. D. Kaplan, S. Ehlert, J. G. Brandenburg, J. P. Perdew, and J. Sun, Workhorse minimally empirical dispersion-corrected density functional with tests for weakly bound systems: r^2 SCAN + rVV10, *Phys. Rev. B* **106**, 075422 (2022).
- [46] J. Kim, A. D. Baczewski, T. D. Beaudet, A. Benali, M. C. Bennett, M. A. Berrill, N. S. Blunt, E. J. L. Borda, M. Casula, D. M. Ceperley *et al.*, QMCPACK: An open source *ab initio* quantum Monte Carlo package for the electronic structure of atoms, molecules and solids, *J. Phys.: Condens. Matter* **30**, 195901 (2018).
- [47] P. R. C. Kent, A. Annaberdiyev, A. Benali, M. C. Bennett, E. J. Landinez Borda, P. Doak, H. Hao, K. D. Jordan, J. T. Krogel, I. Kylänpää *et al.*, QMCPACK: Advances in the development, efficiency, and application of auxiliary field and real-space variational and diffusion quantum Monte Carlo, *J. Chem. Phys.* **152**, 174105 (2020).
- [48] R. Jastrow, Many-body problem with strong forces, *Phys. Rev.* **98**, 1479 (1955).
- [49] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* **140**, A1133 (1965).
- [50] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo *et al.*, QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- [51] M. C. Bennett, C. A. Melton, A. Annaberdiyev, G. Wang, L. Shulenburger, and L. Mitas, A new generation of effective core potentials for correlated calculations, *J. Chem. Phys.* **147**, 224106 (2017).
- [52] A. Annaberdiyev, G. Wang, C. A. Melton, M. C. Bennett, L. Shulenburger, and L. Mitas, A new generation of effective core potentials from correlated calculations: *3d* transition metal series, *J. Chem. Phys.* **149**, 134108 (2018).
- [53] J. Ahn, I. Hong, G. Lee, H. Shin, A. Benali, and Y. Kwon, Energetic stability of free-standing and metal-supported borophenes: Quantum Monte Carlo and density functional theory calculations, *J. Phys. Chem. C* **124**, 24420 (2020).
- [54] M. C. Bennett, J. Ahn, A. Pham, G. Wang, P. Ganesh, and J. T. Krogel, Magnetic measures of purity for MnBi_2Te_4 , [arXiv:2204.04268](https://arxiv.org/abs/2204.04268).
- [55] J. Ahn, S.-H. Kang, M. Yoon, P. Ganesh, and J. T. Krogel, Stacking faults and topological properties in MnBi_2Te_4 : Reconciling gapped and gapless states, *J. Phys. Chem. Lett.* **14**, 9052 (2023).
- [56] C. Lin, F. H. Zong, and D. M. Ceperley, Twist-averaged boundary conditions in continuum quantum Monte Carlo algorithms, *Phys. Rev. E* **64**, 016702 (2001).
- [57] C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, Alleviation of the fermion-sign problem by optimization of many-body wave functions, *Phys. Rev. Lett.* **98**, 110201 (2007).
- [58] I. Hamada and M. Otani, Comparative van der Waals density-functional study of graphene on metal surfaces, *Phys. Rev. B* **82**, 153412 (2010).
- [59] D. Yuan, Y. Zhang, W. Ho, and R. Wu, Effects of van der Waals dispersion interactions in density functional studies of adsorption, catalysis, and tribology on metals, *J. Phys. Chem. C* **124**, 16926 (2020).
- [60] U. Ryde, R. A. Mata, and S. Grimme, Does DFT-D estimate accurate energies for the binding of ligands to metal complexes? *Dalton Trans.* **40**, 11176 (2011).
- [61] D. G. A. Smith and K. Patkowski, Benchmarking the CO_2 adsorption energy on carbon nanotubes, *J. Phys. Chem. C* **119**, 4934 (2015).
- [62] H. Schröder, J. Hühnert, and T. Schwabe, Evaluation of DFT-D3 dispersion corrections for various structural benchmark sets, *J. Chem. Phys.* **146**, 044115 (2017).
- [63] G. Kliche, Far-infrared and x-ray investigations of the mixed platinum dichalcogenides $\text{PtS}_{2-x}\text{Se}_x$, $\text{PtSe}_{2-x}\text{Te}_x$, and $\text{PtS}_{2-x}\text{Te}_x$, *J. Solid State Chem.* **56**, 26 (1985).
- [64] B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, and S. Alvarez, Covalent radii revisited, *Dalton Trans.*, 2832 (2008).
- [65] A. van Bondi, van der Waals volumes and radii, *J. Phys. Chem.* **68**, 441 (1964).
- [66] <http://energy.gov/downloads/doe-public-access-plan>.