Additional info to: Interlayer Coupling in 2D MoS_2 and Phosphorene Bilayers: Benchmark Quantum Monte Carlo Study of Interaction Energies and Quasiparticle Band Gaps

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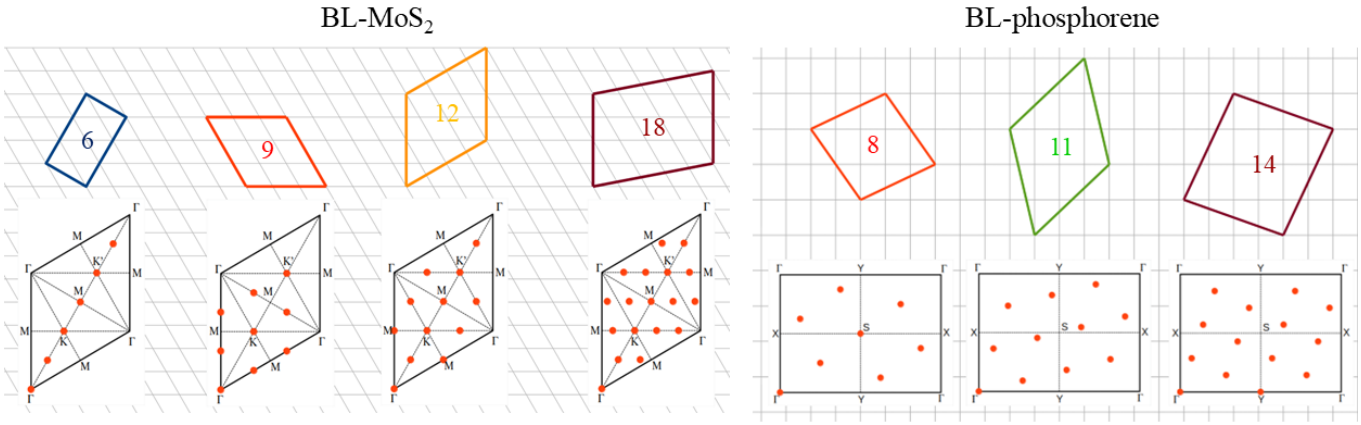


Supplementary Figure 1. Upper panels: Various structural supercells sizes considered for finite-size scaling: 6, 9, 12, and 18 primitive unit cells were used for BL-MoS_2 and 8, 11, and 14 primitive unit cells were used for BL-phosphorene. Lower panels: Corresponding BZs and folding of k-points within different supercells for BL-MoS_2 and BL-phosphorene.

I. DETAILS OF QMC CALCULATIONS

All calculations are in principle reproduceable using the technical details given below.

The atomic structures of the bilayers (BLs) were optimized at the generalized gradient approximation (DFT-PBE)[1] level with the vdW interactions treated at the DFT-D2 level[2].

An electronic excitation from the ground state at a given $\vec{k}$-point was formed into the lowest excited state at a chosen $\vec{k}'$-point and the corresponding excitation, $\Delta^{\rm qp}$, was calculated as singlet-singlet vertical excitation energy,

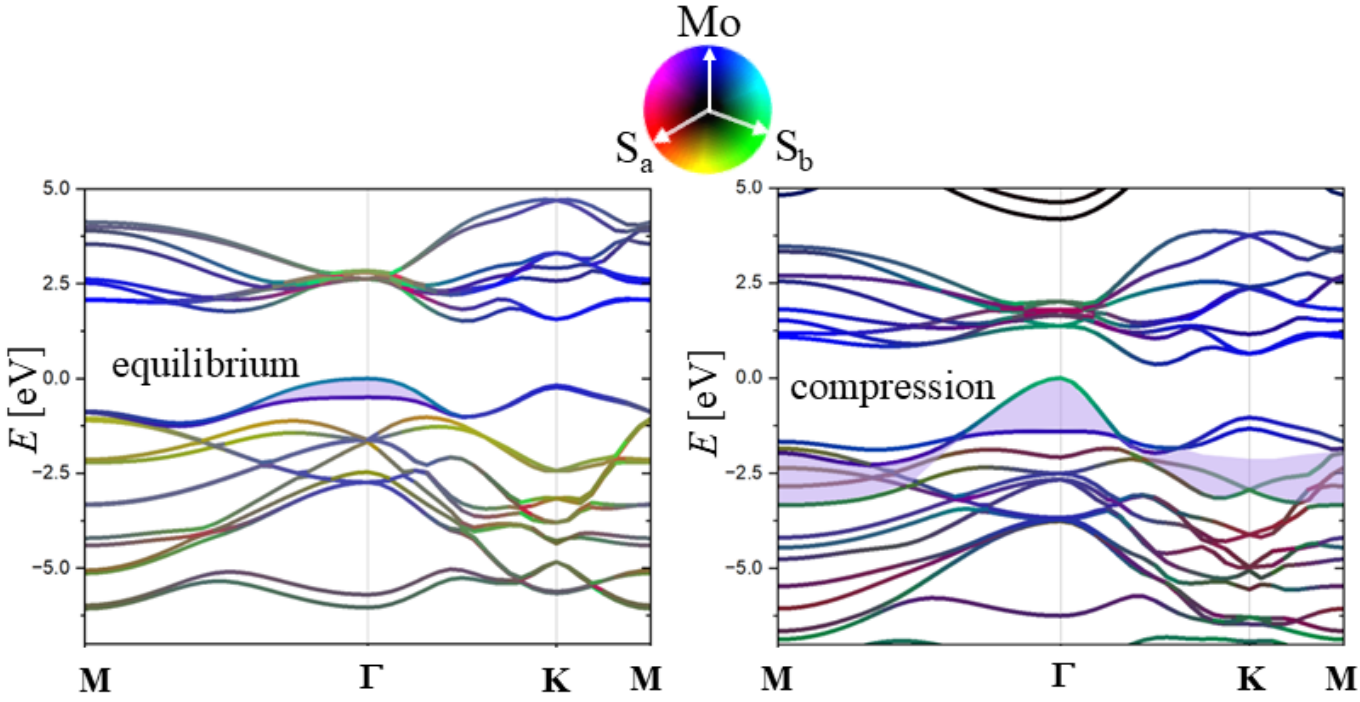
$$\Delta^{\rm qp}_{\vec{k}\to\vec{k}'} \approx E^{\rm ss}_{{\rm v},\vec{k}\to\vec{k}'} = E^{1,{\rm s}}_{\vec{k}\to\vec{k}'} - E^{0,{\rm s}} \quad , \tag{1}$$

with $E^{0,{\rm s}}/E^{1,{\rm s}}_{\vec{k}\to\vec{k}'}$ being the ground-/first excited-states at $\vec{k}/\vec{k}'$ points, respectively. These excitations correspond to quasiparticle gaps[3–5]. We use periodic setups where $E^{0,{\rm s}}/E^{1,{\rm s}}_{\vec{k}\to\vec{k}'}$ were computed by the diffusion Monte Carlo (DMC) method in fixed-node approximation using variational Monte Carlo (VMC) trial wave functions with the nodal hypersurfaces determined by DFT orbitals using the generalized gradient approximation DFT-PBE[1], fully converged with respect to the $\vec{k}$-points, with short-range correlations described by the Jastrow factor[6]. The atomic cores were replaced by Effective Core Potentials[7].

Finite-size scaling was performed for a series of periodic supercells, see Fig. 1, with $N/N_e = 6/312$, $9/468$, $12/624$, and $18/936$ supercells for MoS_2 bilayer. In phosphorene, based on $N/N_e = 8/320$, $11/440$, and $14/560$ supercells, only very weak scaling was found and the result from the $11/440$ supercell was considered as converged. The supercells, the corresponding Brillouin zones (BZ) and folding of $\vec{k}$-points within different supercells is shown in Fig. S 1. Each larger supercell contains also $\vec{k}$-points of the smaller supercell. In both systems linear scaling with $1/N$ was assumed[3]. The effect of spin-orbit couplings was considered small[5] on the energy scale relevant here and neglected.

QMC calculations were performed with the `QMCPACK` suite of codes[8]. All DFT calculations were done with the `Quantum Espresso` package[9].

Generation of the first-order corrected VMC wavefunctions, Eq. (4) of the main text, uses a modified QMCPACK code[8] which can be obtained from the corresponding author upon request.



Supplementary Figure 2. Comparison of DFT band structure of BL-MoS_2 at equilibrium interlayer distance, d_{eq}, and in compression ($d = 5.4$ Å). The color wheel determines the projections onto Mo atoms, S_b/S_a bonding/antibonding orbitals on sulfur atoms. The colored bands depict the spread of the relevant bands throughout the Brillouin zone.

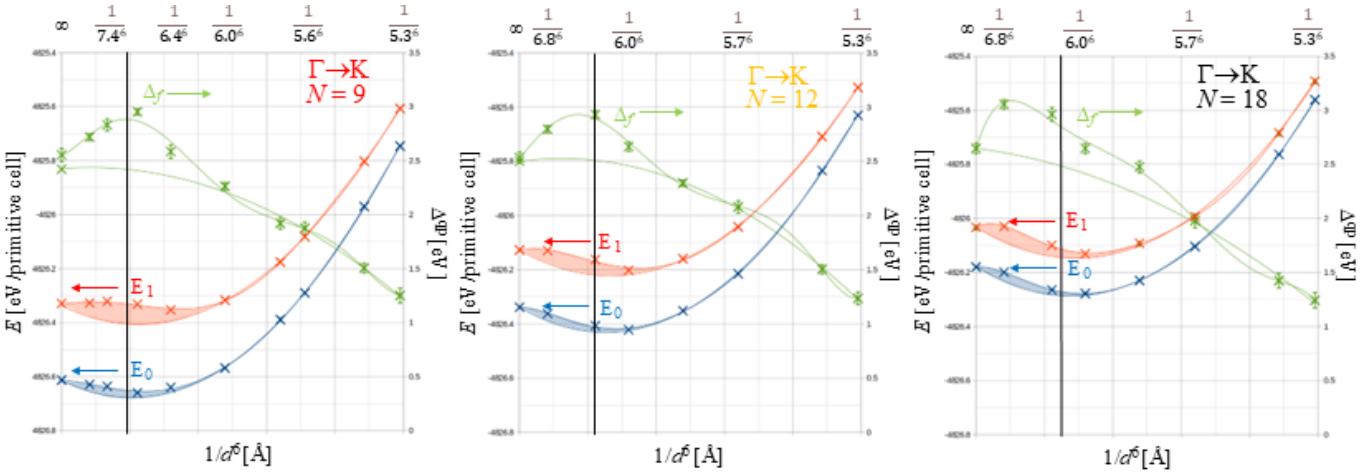
II. DETAILS OF BL-MOS_2 MODELING

Fig. S 2 compares DFT-PBE band structures of BL-MoS_2 calculated at equilibrium and in strong compression ($d = 5.4$ Å). From this comparison it follows that the pair of HOMO/HOMO-1 bands in compression is much more spread out in the Brillouin zone and hence, much less spread in real space. The band structure in compression is much more akin to that in phosphorene, meaning that smaller supercell sizes will describe the system in compression better than in equilibrium.

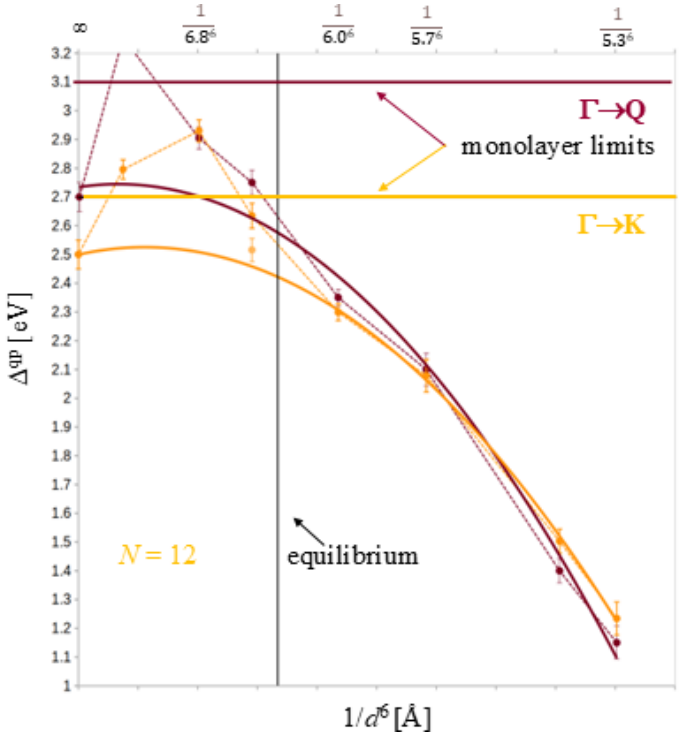
Fig. S 3 provides insights complementary to those shown in Fig. 3 of the main text which shows only the bandgaps, whereas Fig. S 2 reveals also the ground- and excited-states energies and their parabolic fits for N = 9, 12, and 18 supercells for the $\Gamma \to$ K excitation. We note that the results for N = 18 supercell are significantly less accurate (and therefore not used in the main text) and here serve only for qualitative insights.

From Fig. S 3 it is evident that both ground- and excited states are plagued by deviations from quadratic behavior, albeit the excited states significantly more. Furthermore, the deviations become less pronounced with increasing N, but the weakening is only insignificant between N = 12 and N = 18.

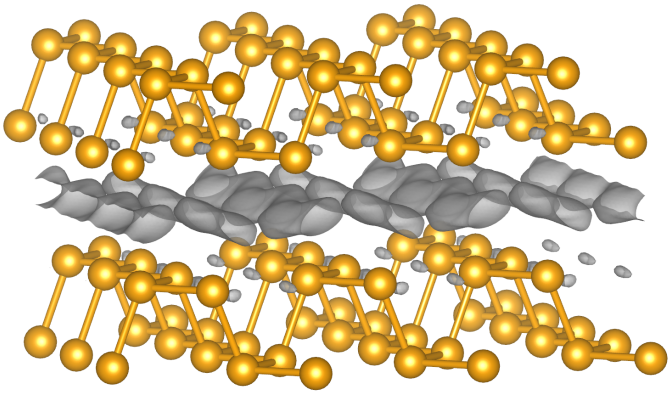
Fig. S 4 shows the quadratic fit of FNQMC $\Delta^{\mathrm{qp}}(d)$ for the $\Gamma \to$ Q excitation calculated in the N = 12 supercell. This result is to be compared with Fig. 3 of the main text for the $\Gamma \to$ K excitation. From the comparison it follows that $\Delta^{\mathrm{qp}}(d)$ for the $\Gamma \to$ Q excitation has a stronger derivative and extrapolates ($d \to \infty$) to a larger value. Hence, we conjecture that also at equilibrium $\Delta^{\mathrm{qp}}_{\Gamma\to\mathrm{Q}}$ is larger than $\Delta^{\mathrm{qp}}_{\Gamma\to\mathrm{K}}$, the band gap of BL-$MoS_2$.



Supplementary Figure 3. Distance dependence of ground- ($E_0(d^{-6})$), excited-state energy ($E_1(d^{-6})$), and quasiparticle gap ($\Delta^{\rm qp}(d^{-6})$) for the Γ →K excitation on supercell size with nodal hypersurfaces corresponding to DFT-PBE without any additional treatment, i.e. Eq. (1) of the main text. Note the deviations from a parabolic behavior, Eq. (3) of the main text. The error bars on the energy curves are of the order of the points.



Supplementary Figure 4. Comparison of $\Delta^{\rm qp}(d^{-6})$ for the Γ →K and Γ →Q excitations for the N=12 supercell.



Supplementary Figure 5. Charge density induced by interaction of monolayers in BL-phosphorene in DFT-PBE-D2 modeling.

III. DETAILS OF BL PHOSPHORENE MODELING

Fig. S 5 shows the DFT-D2 induced charge density in BL-phosphorene due to the interaction of the monolayers. This figure is to be compared with Fig.1 of the main text which shows the FNQMC counterpart. The FNQMC and DFT-D2 induced charge densities are completely different. In particular, at variance with the FNQMC result, the DFT-D2 result does *not* exhibit any charge-transfer interlayer interaction.

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