Quantitative determination of interlayer electronic coupling at various critical points in bilayer MoS$_2$

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In the current topic of van der Waals hetero- and homobilayers, the interlayer electronic coupling plays a critical role in determining the electronic structures of the bilayer as a whole [1–7]. Active control of interlayer coupling through moiré superlattices (MSLs) has emerged as a powerful tool for tailoring electronic structures in twisted bilayer graphene and transition metal dichalcogenide homo- and heterobilayers. However, a largely unexplored factor is the interlayer distance $d$, which can impact the interlayer coupling strength exponentially. In this paper, we quantitatively determine the coupling strengths as a function of interlayer spacing at various critical points of the Brillouin zone in bilayer MoS$_2$. The exponential dependence of the coupling parameter on the gap distance is demonstrated. Most significantly, we achieved a 280% enhancement of $K$-valley coupling strength with an 8% reduction of the vdW gap, pointing to a strategy for designing a unique electronic system in vdW bilayers.

DOI: 10.1103/PhysRevB.106.125302

I. INTRODUCTION

Tailoring interlayer coupling has emerged as a powerful tool to tune the electronic structure of van der Waals (vdW) bilayers. One example is the usage of the “moiré pattern” to create controllable two-dimensional electronic superlattices through the configurational dependence of interlayer electronic couplings. This approach has led to some remarkable discoveries in twisted graphene bilayers, and transition metal dichalcogenide homo- and heterobilayers. However, a largely unexplored factor is the interlayer distance $d$, which can impact the interlayer coupling strength exponentially. In this paper, we quantitatively determine the coupling strengths as a function of interlayer spacing at various critical points of the Brillouin zone in bilayer MoS$_2$. The exponential dependence of the coupling parameter on the gap distance is demonstrated. Most significantly, we achieved a 280% enhancement of $K$-valley coupling strength with an 8% reduction of the vdW gap, pointing to a strategy for designing a unique electronic system in vdW bilayers.

In this work, by using $2H$-stacked bilayer MoS$_2$ (without MSL effect) as a model system, we report quantitative determination of interlayer coupling strength as a function of the interlayer spacing at different critical points of the Brillouin zone. The usage of $2H$-stacked bilayer MoS$_2$ removes fabrication uncertainties associated with mechanical stacking of bilayers [18,25], making the data interpretation and extraction of coupling energy more straightforward. It also removes the lateral configuration variations in a MSL and allows one to assess the coupling as a function of layer spacing independently. By applying hydrostatic pressure in a diamond anvil cell up to 12.7 GPa, the interlayer spacing is changed from 0.62 to 0.57 nm, representing an 8% change. The coupling strength at various critical points is probed using a combination of differential reflectivity (DR) and photoluminescence (PL) spectra from which the exponential decay constants of the interlayer coupling at different critical points are determined. We further compare the results with the $ab$ initio calculations and find that all the results of $K$, $Q$, and $\Gamma$ points agree well with the DFT calculations. Importantly, after reducing the interlayer distance by 8%, the $K$-valley coupling strength is enhanced.
from 36 to 101 meV, representing a 280% enhancement. This result also points to a very promising strategy for designing novel quantum structures based on vdW bilayers.

II. RESULTS AND DISCUSSION

Conceptually, the interlayer electronic coupling in vdW bilayers can be described by a $2 \times 2$ Hamiltonian $H = \begin{bmatrix} \epsilon_1 & t \\ -t & \epsilon_2 \end{bmatrix}$, where $\epsilon_1$ ($\epsilon_2$) is the single-particle energy level of the lower (upper) layer prior to coupling and $t$ is the coupling strength (also referred to as the interlayer hopping integral). A larger coupling strength $t$ and/or a smaller energy difference ($\epsilon_1 - \epsilon_2$) can lead to a larger energy splitting of the hybridized states. This model was successfully applied recently to capture the interlayer hybridization in commensurate heterobilayers [20]. Crucially, the coupling strength $t$ depends on several factors, i.e., the stacking configuration [19,20], the interlayer spacing $d$, and the critical point of the Brillouin zone. Due to the different projected atomic orbitals at different critical points, one expects to observe different coupling strengths at the different projected atomic orbitals at different critical points [32–34]. At $K_v$, the energy separation between $X_A$ and $X_B$ excitons in the DR spectrum can be used to determine the $d$ dependence of interlayer coupling [20]. The PL transition $X_T$ from the lower $Q_C$ state and the upper $\Gamma_V$ state (an indirect transition) can be used to determine the $d$ dependence of interlayer coupling at $Q_C$ and $\Gamma_V$. Some early studies have reported pressure tuning of the band gap in bilayer MoS$_2$ and WSe$_2$ up to $\sim 2-5$ GPa [48–50], indicating that interlayer coupling indeed depends on interlayer spacing. Here, we quantitatively determine coupling strength at various critical points, in which the magnitude and exponential dependence of $t$ are independently demonstrated. Our results are particularly useful for vdW bilayers consisting of monolayers with different chalcogen atoms such as MoS$_2$/WSe$_2$, where the lattice corrugation and/or structure reconstruction effects can result in a more than 20% modulation of the vdW gap [29].

Experimentally, we exfoliate the MoS$_2$ sample directly onto the diamond surface [Figs. 1(d) and 1(e)], where the monolayer, bilayer, and bulk regions can be identified by optical contrast and second harmonic generation measurements. The compressive pressure is uniformly transferred by the inert gas Ne medium. Due to the weak interlayer vdW force, the applied pressure leads to much greater compression along the out of plane direction [51], generating a quasivertical compressive strain on the 2D sample and resulting in a reduced interlayer spacing $d$. We use the lattice parameters obtained by x-ray diffraction (XRD) of thicker MoS$_2$ samples under pressure [51] to convert the pressure dependence to the interlayer spacing dependence.

Exciton resonances in MoS$_2$ monolayers and bilayers occur at the $K$ valley and exhibit large oscillator strength. As shown in Fig. 2(a), for a monolayer MoS$_2$, the spin splittings of the conduction band ($\lambda_C$) and valence band ($\lambda_V$) result from the spin-orbital coupling of the transition metal atoms [38,52,53]. The band splitting for bilayer and multilayer systems is further enhanced by the interlayer coupling, which is determined by the stacking configuration, band alignment, and valley spin [19,20]. For a $2H$-stacked bilayer [Fig. 2(b)], the coupling strength is zero (finite) for the conduction (valence) band edge [19,20]. In this context, the valence band splitting of the bilayer becomes $2\sqrt{\lambda_C^2 + \lambda_V^2}$, which can be accessed optically. For example, two excitonic absorptions of the $K$ valley (known as $X_A$ and $X_B$ excitons) are typically observed in the DR spectra [54–56]. Since $2\lambda_c$ is much larger than $2\lambda_v$ [38,52,53], the energy difference between two bright excitons $\Delta E \equiv X_B - X_A$ becomes a good measure of the valence band splitting $2\lambda_v \left(2\sqrt{\lambda_C^2 + \lambda_V^2}\right)$ for monolayer (bilayer) MoS$_2$ (also see Note S1 in the Supplemental Material [35]).

Figures 2(c) and 2(d) show the DR spectra of monolayer and bilayer MoS$_2$ with applied compressive pressure,
respectively. While \( \Delta E = -2\lambda_V \) of the monolayer is nearly independent of pressure, we find that \( \Delta E = -(2\sqrt{\lambda_V^2 + t^2}) \) of the bilayer increases significantly with the applied pressure, demonstrating that \( t \) is increasing. Figure 3(a) summarizes the pressure-dependent \( \Delta E \). Under applied pressure, the exciton energy difference \( \Delta E \) of bilayer MoS\(_2\) exhibits a nonlinear increase, while that of monolayer MoS\(_2\) remains almost unchanged. The significant difference between them demonstrates the pressure-dependent interlayer electronic coupling. For the monolayer sample, we notice that there are rigid \( X_A \) and \( X_B \) peak blueshifts (~20 meV) between zero and 1.9 GPa, which may be caused by strain-induced changes in band gap energy [51]. However, since our approach relies on energy difference, the influence of band gap energy has been largely eliminated. Based on the model, we extracted the coupling strength \( t(KV) \) as a function of pressure, as displayed in Fig. 3(b) (also see Note S2 in the Supplemental Material [35]). At the highest applied pressure (12.7 GPa), we determined a coupling strength \( t(KV) = 101 \text{ meV} \), which is ~280% greater than the value found at zero pressure \( t(KV) = 36 \text{ meV} \). We also observe that \( t(KV) \) exhibits an increasing slope at larger pressures.

Here we use the lattice parameters obtained by XRD of the thicker MoS\(_2\) sample under pressure [51] to convert the pressure dependence to the \( d \) dependence, as shown in Fig. 3(c). In Fig. 3(d), we compare the experimental results (dots) with the spacing-dependent \( t \) extracted from the band structure calculations (blue line, DFT-1). In this calculation, we only change the interlayer spacing \( d \) and keep the in-plane lattice as a constant. It is clear that the coupling strength \( t(KV) \) exhibits an exponential growth as a function of \( d \). The results are fitted by an exponential function \( t(KV) = t(KV)_0 e^{-(d-d_0)/\lambda_0} \), with the equilibrium spacing \( d_0 = 0.6165 \text{ nm} \). We determine \( t(KV)_0 = 34 \text{ meV} \) (42 meV) and \( \lambda_0 = 0.046 \text{ nm} \) (0.070 nm) for the experimental (DFT-1) data. The discrepancy between the experimental and DFT results cannot be neglected; especially the fact that the decay length differs by about 34% (also see Tables S1 and S2 in the Supplemental Material [35]).

We realize that this difference arises from the effect of in-plane lattice compression, which occurs simultaneously when hydrostatic pressure is applied [51]. Based on the XRD data, we include both the in-plane and out of plane lattice compression in the calculation (red line, DFT-2). Clearly, after considering the effect of in-plane lattice compression, the calculations fit the experimental data much better. We obtain...
parameters of \( t^{(k_V)} = 41 \text{ meV} \) and \( \lambda^{(k_V)} = 0.054 \text{ nm} \), which are only \( \sim 15\% \) different from the experimental data. Therefore, our results demonstrate that both in-plane and out of plane lattice compression can enhance the interlayer coupling strength, with the latter playing a major role. The reason can be readily understood from the view of orbital wave function overlap. Both in-plane and out of plane compression can bring the Mo atoms of the adjacent layer closer, resulting in higher wave function overlap and greater coupling strength.

We further evaluate the coupling strength at other valleys using the pressure-dependent PL spectra of bilayer MoS\(_2\) [Fig. 4(a)]. The PL spectra feature two peaks, one from the direct \( K\)-\( K\) exciton and another from the indirect exciton \( X_1 \) \([26,27]\). In stark contrast to the nearly unchanged \( K\)-\( K\) exciton \((X_1)\) energy, the indirect exciton \( X_1 \) exhibits a significant redshift of \( \sim 240 \text{ meV} \) from zero to 6.3 GPa. The PL redshift indicates the shrinkage of the indirect gap under pressure. At pressure higher than 6.3 GPa, the \( X_1 \) indirect exciton emission is no longer detectable. After converting to the interlayer distance dependence, the indirect exciton transition energy as a function of interlayer distance, \( X_1 \) vs \( d \), is plotted in Fig. 4(b). Also shown are DFT calculations for the \( Q_C\)-\( \Gamma_V \) transition (red curve) and \( K_C\)-\( \Gamma_V \) transition (blue curve) as a function of interlayer distance. Interestingly, the energy redshift of \( X_1 \) vs \( d \) shows excellent agreement with the \( Q_C\)-\( \Gamma_V \) transition except for an apparent offset of \( \sim 0.25 \text{ eV} \). This offset is not surprising since DFT calculations often underestimate the band gap \([57]\). Due to the close energy of \( K_C \) and \( Q_C \) points in the conduction band, the PL emission of the indirect gap in bilayer MoS\(_2\) has been under debate \([26,27]\). Our results show that indirect PL emission is mainly from \( Q_C\)-\( \Gamma_V \) excitons \([48]\).

Under applying compressive pressure, the lifting up of the \( \Gamma_V \) point and the pushing down of the \( Q_C \) point both contribute to the shrinkage of the indirect gap [Figs. 1(b) and 1(c)].

Our optical spectroscopy measurements do not independently determine the interlayer coupling at \( Q_C \) and \( \Gamma_V \). Rather, it is a combined effect of \( Q_C \) and \( \Gamma_V \) as a function of \( d \). However, given the fact the experimental result of \( X_1 \) vs \( d \) shows excellent agreement with the calculated result for the \( Q_C\)-\( \Gamma_V \) transition, we can conclude that the calculated results for the interlayer coupling at \( Q_C \) and \( \Gamma_V \) are individually accurate (also see Tables S1 and S2 in the Supplemental Material \([35]\)).

In this context, we are able to extract the coupling strength of the \( Q_C \) and \( \Gamma_V \) points from the DFT calculations using the \( 2\times2 \) Hamiltonian. As shown in Fig. S4 in the Supplemental Material \([35]\), the obtained results also exhibit an exponential dependence on \( d \) and can be fitted by an exponential function, with extracted \( t^{(Q_C)} = 0.067 \text{ nm} \) \((\lambda^{(Q_C)} = 0.108 \text{ nm})\) for \( t^{(\Gamma_V)} \) \((\lambda^{(\Gamma_V)} = 0.067 \text{ nm})\). When the pressure changes from zero to 6.3 GPa, we determine that \( t^{(\Gamma_V)} \) changes from 335 to 522 meV and \( t^{(Q_C)} \) from 192 to 253 meV.

In Tables S1 and S2 in the Supplemental Material \([35]\), we summarize and compare the experimental results with the DFT calculations. We conclude that the coupling strength (decay length) of \( \Gamma_V \) and \( Q_C \) are larger (longer) than that of \( K_V \). This valley-dependent coupling strength is due to the fact that the interlayer hopping integral is affected by the \( p_z \) orbitals of the chalcogen atoms. Since the atomic distances between the inner chalcogen atoms of adjacent layers are the shortest, the large orbital wave function overlap leads to significant \( p_z\)-\( p_z \) hybridization \([58]\). Our results show that the coupling strength is indeed correlated with the \( p_z \)-orbital component of the critical point, i.e., \( p_z \)-orbital components of \( \Gamma_V \), \( Q_C \), and \( K_V \) points are 28\%\((\Gamma_V) > 11\%\((Q_C) > 0\%\((K_V)\), which leads to \( t^{(\Gamma_V)} > t^{(Q_C)} > t^{(K_V)} \). In addition, the decay length exhibits a trend of \( \lambda^{(\Gamma_V)} > \lambda^{(Q_C)} > \lambda^{(K_V)} \), which can also be understood by \( p_z\)-\( p_z \) hybridization. Since the wave function of \( p_z \) orbitals elongates in the \( z \) direction, a less sensitive \( d \) dependence can be expected, which leads to longer decay lengths at \( \Gamma_V \) and \( Q_C \) than that at \( K_V \). On the contrary, the states at \( K_V \) comprise transition metal \( d_{x^2−y^2} \) and \( d_{xy} \) as the majority orbital, and chalcogen \( p_z \) as the minority orbital (see Table S3 in the Supplemental Material \([35]\)), leading to a rapidly decaying wave function along the \( z \) direction and a shorter decay length.

In conclusion, our experiments firmly establish the exponential dependence of the electronic coupling on the interlayer spacing at various critical points of bilayer MoS\(_2\). In particular, we quantitatively determine the coupling strengths of the \( \Gamma_V \), \( Q_C \), and \( K_V \) points, as well as their interlayer spacing dependence. We experimentally demonstrate that, due to the increased overlap of atomic orbital wave functions, interlayer coupling strength can be enhanced by both in-plane and out of plane lattice compression, with the latter playing a major role. By measuring the absorption of \( X_A \) and \( X_B \) excitons, \( t^{(k_V)} \) and its \( d \) dependence are independently determined, which are believed to be free from other factors such as band gap and exciton binding energy. In addition, we demonstrate that by applying a moderate pressure of 12.7 GPa, the interlayer \( K \)-valley coupling can achieve a 280\% enhancement over that in natural bilayers. Through the PL measurement of indirect excitons, we also determine the \( d \) dependence of \( t^{(\Gamma_V)} \) and \( t^{(Q_C)} \). These results have important implications for vdW heterostructures. Tuning the magic angle in twisted bilayer graphene through hydrostatic pressure has recently been demonstrated \([21]\). One therefore expects similar tunability can be achieved in twisted bilayer WSe\(_2\) \([11,12]\). Most
We also acknowledge support from the Welch Foundation (Grants No. F-1672 and No. F-1662), the U.S. NSF (Grant No. DMR-1808751) and the U.S. Air Force (Grant No. FA2386-18-1-4097). C.-R.P., P.-J.C., and M.-Y.C. acknowledge the support from Academia Sinica, Taiwan. W.-H.C. acknowledges the support from the Ministry of Science and Technology of Taiwan (Grant No. MOST-110-2119-M-A49-001-MBK) and the support from the Center for Emergent Functional Matter Science (CEFMS) of NYCU supported by the Ministry of Education of Taiwan. W.-T.H. acknowledges the support from the Ministry of Science and Technology of Taiwan (Grant No. MOST-110-2112-M-007-011-MY3) and the Yushan Young Scholar Program from the Ministry of Education of Taiwan. C.-K.S. also acknowledges the Yushan Scholar Program from the Ministry of Education of Taiwan.

ACKNOWLEDGMENTS

We thank Dr. Suyu Fu and Dr. Xianghai Meng for their help with the diamond anvil cells. This research was primarily supported by the NSF Materials Research Science and Engineering Centers (MRSEC) under Grant No. DMR-1720595. We also acknowledge support from the Welch Foundation and the Yushan Young Scholar Program from the Ministry of Education of Taiwan.


